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The Franklin Institute

DEVOTED TO

SCIENCE AND THE MECHANIC ARTS

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Vol. 194 JULY, 1922 No. 1

CATALYSIS AND CATALYTIC AGENTS IN CHEMICAL PROCESSES.*

BY

HUGH S. TAYLOR.

Associate Professor of Physical Chemistry, Princeton University.

MODERN theoretical chemistry in its conclusions with regard to the structure of atoms and molecules indicates a mode of differentiation of chemical reactions. The mechanism of processes involving ions, oppositely charged, is comparatively simple. It is safe to assume that every time a silver ion meets a chloride ion formation of silver chloride results and in aqueous solution, precipitation ensues when the solution becomes saturated with respect to the salt produced. Reactions between neutral molecules, on the other hand, are by no means so readily initiated nor is the mechanism of reaction so obvious. Even molecules which are oftentimes regarded as " unsaturated " display a marked stability. Ethylene and hydrogen in a clean glass vessel at ordinary temperatures are quite without action on one another. Apparently each molecule under such conditions is a sufficiently stable configuration of negative electrons surrounding positive nuclei that, without special measures, no rearrangement of the electron configurations results. The old method of disturbing the electron configurations of these molecules was to heat the gas mixture. Temperature brings about a more rapid movement of the electrons, positions of instability are more frequently produced, and, conse-

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* Presented at a meeting of the Section of Physics and Chemistry of the Franklin Institute held Thursday, February 23, 1922.

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quently, interaction between the two gases more often occurs. With the aid of a suitable catalytic agent, this effect of increased temperature may be secured at ordinary temperatures. It is only necessary in this case to pass the cold gas mixture over a catalyst composed of nickel obtained by low temperature reduction of nickel oxide. It may be shown that the effect of the nickel is probably to cause, by temporary association of the catalyst with the gas molecules in question, a momentary rearrangement of the electron configuration around the nuclei of the molecules and the consequent production of a higher order of instability in the molecule than normally obtains in the gaseous system, at the given temperature, in the absence of the catalytic agent.

The rôle of the catalyst, therefore, is mainly in that realm of reactions occurring between non-ionized molecules. A moment's thought will show that this includes practically all types of chemical reactions. The ionic reactions are the least affected by catalysts though, even in such, catalytic influences have been found. The influence of the solvent medium is possibly catalytic. Attention may be drawn by way of example to the catalytic influence of manganese sulphate in various titrations with potassium permanganate. The possibilities of the use of the catalyst are legion, on the other hand, in gas reactions, involving oxidation, reduction, halogenation, in the reactions of organic chemistry, hydrolysis and dehydration, substitutions, hydrogenations, dehydrogenations and oxidations whether homogeneous or heterogeneous, in gas-solid and gas-liquid systems. The accelerating influence of manganese dioxide on the decomposition of potassium chlorate shows, too, that one solid may markedly influence the reactivity of another solid. Certain electrochemical processes involving cathodic or anodic reactions are modified as to rate by the presence of catalytic agents. The activity of the enzymes in biochemical processes is also frequently catalytic in nature. Finally radiation, in one or another of its varied forms, whether as light, ultra-violet, visible or infra-red, or as X-rays or as the radiations from radioactive materials, may also function in a catalytic manner.

In all such processes the rôle of the catalytic agent is that of an intermediary, accelerating, or in some cases retarding, the operation of reactions which would normally occur, though at differing rates, in the absence of the catalyst. The accelerating or positive catalysts are those with which the chemist is normally concerned. Occasionally, as in the use of such a substance as acetanilide to stabilize hydrogen peroxide solutions, negative catalysts or retarding agents are utilized. In certain reactions one of the reacting substances or one of the products of the process is a catalyst for the original reaction. Such cases are termed autocatalysis. Thus the decomposition of silver oxide to yield oxygen and silver is catalyzed by the finely divided metallic product. A reaction which may be initially quite slow will in such cases gather momentum as the autocatalyst is produced.

The modification of reaction rate which a true catalyst produces must be attained without change in the chemical form of the catalyst on completion of the reaction cycle. Its participation in the process as an intermediate compound is not excluded; indeed, for many homogeneous catalytic processes it seems necessary to assume the formation of such intermediate compounds. Nevertheless, a true catalytic agent must be regenerated in its original chemical form when the catalytic operation is complete. This being so, it is evident that catalysts will also be characterized by their operation in small concentrations for promotion of reaction between large quantities of the interacting substances. Thus, some recent figures[1] indicate that one square inch of platinum gauze, 0.003 wire and 80 mesh, acting as a catalyst in the oxidation of ammonia, gives a yield of six pounds of nitric acid per day. For the present, also, it seems safer to assume that the catalyst promotes the establishment of the same equilibrium as would normally prevail in the absence of a catalyst. It is true that this viewpoint has been vigorously contested from several quarters in recent years. As yet, however, no unequivocal case of a shift in equilibrium caused by a catalyst has been brought forward, while there are many cases in which the reverse is true.

While the catalyst remains unchanged chemically on completion of the process, the same does not hold true in its physical state. Indeed, in many cases of heterogeneous catalytic reactions the solid catalyst shows marked physical change. The active catalyst is normally a porous, amorphous material and, in process of activation, catalysts tend to assume this form. Manganese dioxide, originally coarsely crystalline, will be found to be an amorphous powder after having catalyzed the decomposition of potassium chlorate. The change is most strikingly manifested in the microscopic examination of platinum gauze before and after use in the oxidation of ammonia. The gauze is converted from a smooth plane-surfaced wire to a corrugated pitted material. This is shown in the accompanying figure. Similar changes in physical form are shown by silver gauze when used for the catalysis of hydrogen oxygen mixtures.

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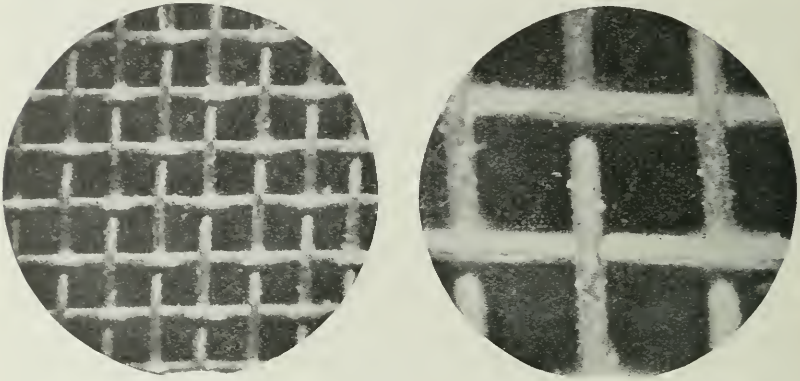
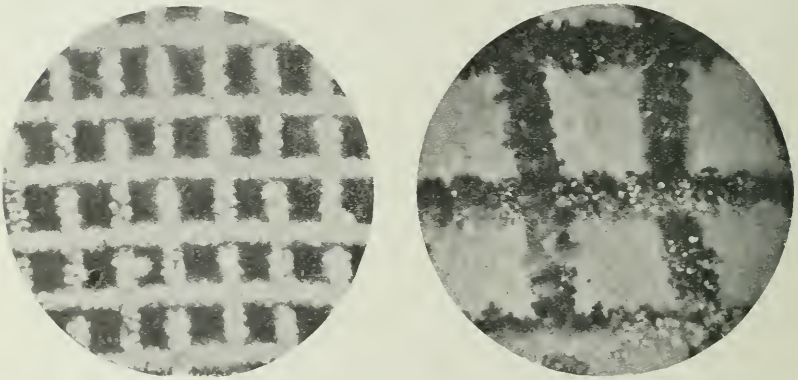
[1] Private communication from Dr. Chas. L. Parsons.

FIG. 1.



X 24
Plain wire before use.

X 75
Plain wire before use.



X 24
After some weeks' use.

X 75
After some weeks' use.

Principles and Methods of Catalytic Investigation.—There appears to be a fairly general impression that the investigation of a catalytic process is a somewhat random occupation and that the discovery of a catalytic agent is a fortuitous result of trial and error with indiscriminate selections from available compounds. It is true that a large number of catalysts have been discovered accidentally, or rather with little basic theory guiding the choice of material to be studied. With accumulation and systematization of facts relative to catalytic agents and the reactions they promote, the study of new processes becomes, however, less and less empirical. In the early days of organic chemistry, the student of a new compound doubtless applied such reagents as sulphuric acid or strong alkali quite empirically in the hope that he might gain the desired information relative to his material. To-day, as a result of accumulated experience he applies these and other catalytic agents consciously, with full knowledge of the normal reactions which they promote. In the same way, the coördination of knowledge in reference to catalytic agents and the reactions they assist gives to the catalytic chemist of to-day more deliberate and purposeful methods of work. A glance at the subjoined

Reaction Process	Type of Catalyst	Exemplification in Industrial Practice.
Hydration and Hydrolysis	Acids	(a) Hydrolysis of glycerides, soap and candle industry, sulphuric, sulphonic (Twitchell reagent) acids as catalysts. (b) Hydrolysis of starches and wood cellulose to yield sugars. Sulphuric, hydrochloric, sulphurous acids as catalysts. (c) Hydrolysis of esters using acids. (d) Hydration of acetylene to yield acetaldehyde. Various acids as catalysts.
	Alkalies	(a) Hydrolysis as in (a) and (c) above. NaOH, KOH, $Ca(OH)_2$, MgO, ZnO as catalysts.
Dehydration	Acids	(a) Manufacture of ether. Sulphuric, sulphonic and phosphoric acids as catalysts. (b) Esterification processes. Hydrochloric and sulphuric acids as catalysts.
	Oxides	(a) Manufacture of ethylene and unsaturated hydrocarbons. Clays, Al_2O_3, SiO_2, TiO_2 as catalysts.
Halogenation	Non-metallic elements	(a) Chlorination of carbon disulphide, carbon monoxide and hydrocarbons. Carbon, iodine, sulphur as contact agents.

	Chlorides	(a) In synthetic organic chemistry. $AlCl_3$, $FeCl_3$, $SbCl_5$, $SnCl_4$, $ZnCl_2$, $HgCl_2$, as contact agents.
Oxidation	Metals, especially the platinum metals	(a) Contact sulphuric acid process using finely divided platinum on a suitable support.
		(b) The oxidation of ammonia using a platinum gauze.
		(c) The preparation of formaldehyde, using copper or silver (see dehydrogenation).
	Oxides	(a) Lead chamber process, employing a gaseous catalyst, oxides of nitrogen.
		(b) Contact sulphuric acid manufacture with iron oxide catalyst.
		(c) Chance-Claus process of sulphur recovery. Oxide of iron as catalyst.
		(d) Purification of illuminating gas. Hydrated oxide of iron as catalyst.
		(e) Surface combustion processes, refractory oxides as catalysts.
		(f) Oxidation of hydrocarbons, V_2O_5, MoO_3, WO_3, etc., as catalysts.
	Salts	(a) Deacon chlorine process, copper chloride as catalyst.
		(b) Oxidation processes in the dye industry. Mercury and copper salts.
		(c) Oxidation of aldehydes, manganese salts as catalysts.
		(d) Drying of oils. Metallic soaps as accelerators.
Hydrogenation	Metals	(a) Hydrogenation of oils. Nickel and platinum as contact agents.
		(b) Fine organic chemical industry, *e. g.*, synthesis of cyclo-hexane, reduction of organic compounds. Nickel as catalyst.
	Oxides	(a) Hydrogenation of oils, nickel oxide as catalyst (especially at elevated pressures).
Dehydrogenation	Metals	(a) Cracking of oils, nickel, copper, iron, aluminium as catalysts.

		(b) Dehydrogenation of alcohols, copper, silver and nickel as catalysts.
	Oxides	(a) Cracking of oils, Al_2O_3 and TiO_2 as catalysts. (b) Dehydrogenation of alcohols, ZnO, SnO, CaO and MgO as catalysts.
Nitrogen Fixation	Metals and metal-oxide mixtures	(a) Ammonia synthesis. Reduced iron, iron-molybdenum, iron-potash, and nickel-sodium as contact agents. (b) Cyanide formation. Reduced iron as catalyst. (c) Arc process of oxide of nitrogen formation. Metal electrodes as negative catalysts. (d) Nitride formation (Serpek process). Iron, copper, chromium, molybdenum, etc., as catalysts.

table of the more important industrial catalytic reactions classified as to type of reaction and as to type of catalyst employed will suggest the method of attack upon a new catalytic problem. It will be clear that the first stage in the investigation is a determination of reaction type, whence the probable type of catalyst will follow. The trained catalytic chemist would spend little time investigating a hydrogenation process using catalysts which normally catalyze say halogenation or dehydration. Each class of reaction has its own class of catalytic agent and each of these classes may similarly be circumscribed as to members. Thus, for example, it may be seen that as catalysts for oxidation processes, oxides are an important class of catalysts. Of the oxide class, however, it is remarkable that only a limited number function at all prominently as catalysts. The oxides of well-defined stability are conspicuously absent. The oxides of the alkali metals, to a less extent those of the alkaline earths, definite irreducible oxides such as magnesium oxide and aluminium oxide are not frequently to be found among the oxide catalysts of oxidation. On the other hand, the labile oxides such as those of iron, copper, manganese, silver, vanadium, tungsten, molybdenum uranium, chromium, cobalt and cerium are frequently to be noted in a systematic study of such oxide catalysts of oxidation. In view of what has been said with regard to the catalyst as promoter of electronic instability in the reacting molecules, it is interesting to observe that this large class of catalytic agents is made up of compounds of elements which all show a ready tendency to modify the configuration of electrons surrounding their positive nuclei. In the older nomenclature they are the oxides of polyvalent metals. It is undoubtedly due to this variability of electronic configuration that their oxidation activity is due. In a similar manner other types of reaction and other classes of catalysts may be treated. The result of such considerations is a studied and orderly choice of reaction catalysts.

It is advantageous, also, to remember that, in normal circumstances, a catalyst accelerates both the forward and the backward reactions of an equilibrium process. The catalyst of hydrogenation should therefore be, and is, frequently, the catalyst of dehydrogenation processes. Nickel assists the direct hydrogenation of benzene; it is also the catalyst for the dehydrogenation of cyclo-hexane. Since it has been observed, in the reduction of nitrobenzene by hydrogen in the presence of nickel, that reaction may proceed further than the aniline stage and yield benzene and ammonia, it naturally suggests itself to the catalytic chemist that nickel will catalyze the removal of hydrogen from benzene and ammonia to yield aniline. This has been shown to be true,[2] though the yields attained are exceedingly small.

Correct appreciation of such principles and suitable correlation with known facts frequently results in the forecasting of suitable catalytic agents. There is at the present time in the development stage a catalytic process of immense industrial potentialities, concerning which details are as yet carefully withheld. The process involves the treatment of water-gas ($H_2 + CO$) with catalytic agents to yield methyl alcohol. The reaction may be formulated by means of the equation

$$CO + 2H_2 = CH_3OH.$$

The process probably takes place through formaldehyde as an intermediate product which is then immediately hydrogenated to methyl alcohol.

$$CO + H_2 = HCHO.$$

$$HCHO + H_2 = CH_3OH.$$

The essential reactions are hydrogenations and call therefore in all probability for reduced metals as catalysts. The knowledge that nickel, cobalt and palladium cause the hydrogenation of carbon monoxide to proceed to methane and water

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[2] Meyer and Tanzen, Ber., **46**, 3198 (1913).

$$CO + 3H_2 = CH_4 + H_2O$$

seems to rule these catalysts out of court in the reaction under consideration. The knowledge that copper and platinum are incapable of promoting the conversion of carbon monoxide to methane brings them therefore prominently into consideration. The knowledge that copper is an active agent for the dehydrogenation of methyl alcohol to yield formaldehyde is additional evidence in favor of a trial of reduced copper as the catalyst. The information which would permit a test of such a forecast has not been disclosed but it should not long be delayed.

A prior knowledge of the equilibrium conditions in the reaction to be catalyzed is an extremely valuable asset to the catalytic investigation. The technical success that has been attained in the contact sulphuric acid process, in the synthesis of ammonia and in the water-gas catalytic process of hydrogen manufacture for ammonia synthesis is based, in no small measure, on the equilibrium data accumulated by the Badische Anilin and Soda-Fabrik and associated investigators. These data define the optimum working conditions and facilitate the definition of working efficiencies. These processes are at once classical examples of the contributions of catalysis to modern chemical industry and justification of the claims of theoretical science upon the support of the technical man.

In the absence, however, of exact equilibrium data, useful approximations may be made. The Nernst approximation[3] formula is especially useful and applicable. Nor can the conclusions of thermodynamics be neglected by the catalytic chemist in the definition of the operating conditions. Thus, in the reaction already discussed,

$$CO + 2H_2 = CH_3OH$$

the reaction is exothermic. Low temperatures therefore favor the formation of methyl alcohol. Pressure facilitates its production in higher concentration at a given temperature. The upper limit of temperature for economically feasible yields may be computed with the aid of the approximation formula of Nernst.

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[3] See Lewis, "System of Physical Chemistry," vol. ii, 1919, pp. 75 and 330, *et seq.*

The Form of the Catalyst; Catalyst Support Materials.—In homogeneous media the form of the catalyst is not important. A gaseous catalyst in a gas reaction or a dissolved catalyst in liquid systems has a definite and readily reproducible form. In the last analysis the acceleration or retardation caused by the catalyst is, in such systems, proportional to its concentration. This point is not infrequently forgotten owing to deviations from strict proportionality between reaction velocity and presumed concentration. Thus, as is well known, the catalytic action of acids in hydrolytic processes is not strictly proportional to the molar concentration of the acid catalyst. Such abnormalities have been the object of much study. Better concordance is obtained between hydrogen ion concentration and catalytic activity, but even there the proportionality is not an exact one. Various reasons for this fact have been adduced, none completely satisfactory. By some it is urged that the undissociated acid molecule is catalytically active; by others that only non-hydrated hydrogen ions are catalytically active. Others define the catalysis in terms of the thermodynamic "activity" of the ions. Concerning all such, whatever the real explanation, it may be remarked that the catalysis in homogeneous media will be proportional to the active mass of the actual catalyst or catalysts, since there may be several present.

If the catalytic reaction be heterogeneous, the form of the catalyst becomes immediately a matter of first importance. That this is so in liquid-liquid systems may be shown in reference to hydrolytic processes. In homogeneous media it is well known that the reaction velocity of hydrolysis of esters is approximately proportional to the hydrogen ion concentration. In heterogeneous systems, however, the acid strength is not the principal factor. Thus, hydrochloric acid is not so good an agent for the splitting of fats as the sulphonic acids, though these acids are approximately of equal strengths. The activity of the sulphonic acids is modified profoundly by the nature of the hydrocarbon grouping, as was early shown by Twitchell. The Twitchell reagent, naphthalene stearo-sulphonic acid or a similarly constituted acid, undoubtedly owes its efficiency as a hydrolytic agent in the splitting of fats to the fact that the molecule of acid catalyst is orientated, so that the polar sulphonic grouping is in the aqueous medium, while the hydrocarbon nucleus is within the glyceride oil. This is a splendid instance of technical development far in advance of scientific theory. It will be seen that the concept of orientation of molecules as a necessary feature of contact action is of quite recent origin.

In the case of solid contact agents, the problem of form is equally important. The striking feature common to most of the contact catalysts is their porous or finely divided structure. The successful contact agent is characterized by this amorphous nature of the material. As already emphasized in this connection, with platinum and silver gauze catalysts, the preliminary phase of activation is accompanied by a change in the surface form of these metals to a roughened surface with which catalytic activity is high. This change may operate favorably to catalysis in two ways. It may change the normal spacing of the atoms in the metal surface to one more favorable for the adsorption of the reacting gas molecules in such configurations as are conducive to interaction. In addition, however, the activation may result in the production of a larger number of atoms in the surface layer, with electrons in a more or less unsaturated or free condition unshared by neighboring atoms and able, therefore, to enter into association with impinging molecules more readily than the symmetrically placed atoms in a non-catalytic surface. Evidence of this phenomenon is forthcoming from adsorption experiments[4] with catalytic agents in the Princeton laboratories. Nickel obtained by reduction at low temperatures (200–300° C.) shows high absorption for many gases. The extent of adsorption, however, is determined largely by the previous history of the catalyst. By submitting the catalyst to temperatures between 300–600° C. the nickel will slowly lose its adsorptive power, presumably by saturation of the free electrons of the nickel atoms with neighboring nickel atoms, which process is, of course, the phenomenon of crystallization. It is undoubtedly this same phenomenon which accounts for the slow loss of activity of a catalyst with prolonged use, even though reactants of the utmost purity be used.

The loss of adsorptive power by nickel, parallels the variation in catalytic power of this metal with variation in temperature of preparation. Kelber[5] showed that nickel oxide *per se,* when reduced at about 300° C., gave a moderately active catalyst, but when reduced at 450° C., gave a product of but feeble activity. The conclusions have recently been checked by Armstrong and Hilditch, who show that reduction at higher temperatures gives rise to considerable shrinkage in the volume of the catalyst.

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[4] See Taylor and Burns, *Journ. Amer. Chem. Soc.*, 43, 1273 (1921).

This shrinkage and loss of catalytic activity can be largely suppressed if the active material is spread upon an inert support. In this way, for example, it is possible to produce at 500° C. a nickel catalyst supported upon kieselguhr, of greater activity than from precipitated nickel hydroxide, by reduction at 300° C. The kieselguhr, which does not shrink on heating, almost wholly determines the bulk of the product and the nickel adhering to the support can only coalesce with much greater difficulty. The factors in these several cases are well set forth in the following chart, due to Armstrong and Hilditch:

Source of Reduced Nickel				Reduced Nickel		
	Density	Apparent Volume c.c.	Temperature of Reduction	Density	Apparent Volume c.c.	Catalytic Activity
Powdered fused oxide	6.96	0.35	500° C.	8.14	0.52	None
Precipitated hydroxide	5.41	0.87	(300° C.)	7.85	0.83	Fair
			(500° C.)	8.18	0.56	Very little
On kieselguhr	1.63	3.22	500° C.	1.85	2.67	Very active

Recent measurements by Mr. A. W. Gauger in the Princeton laboratories have shown that the adsorption of nickel, *spread on kieselguhr,* is the same when the catalyst is reduced at 500° C. as when reduction is effected at 300° C. in sharp contrast to the behavior of "unsupported" nickel. Concordance is, therefore, shown between these adsorption measurements and the catalytic studies of Kelber, Armstrong and Hilditch. It has been shown, further, that the extent of adsorption of gas by unit weight of metallic catalyst is enormously increased when the catalyst is spread on a porous support. Thus, one gram of nickel spread on diatomite (Nonpareil) brick adsorbs the quantities of hydrogen listed in the tables below, where also are to be found corresponding figures for nickel obtained by reduction of coarsely powdered nickel oxide, prepared by ignition of the nitrate.

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[5] Ber., **49**, 55, 1868 (1916).

Catalyst	C.c.s Hydrogen Gas Adsorbed per gram Ni, at							
	25°	80.5°	175°	184°	200°	218°	250°	305° C.
Nickel without support	0.69	0.63	....	0.53	....	0.48	....	0.36
	....	....	5.2	....	5.1	....	4.73	....

Our researches have enabled us to show also a striking parallelism between adsorptive capacity and catalytic activity in a variety of cases, though this is not the only factor involved, as will later be shown. Nevertheless, the results obtained, and those cited previously, demonstrate the important part which the catalyst support material may play in successful catalysis. With expensive catalytic agents, as, for example, platinum, the use of a support is frequently indispensable.

A variety of materials has been employed as catalyst supports. Platinum is normally employed in the contact sulphuric acid process, either on asbestos fibre or on calcined magnesium sulphate, the platinum being generally sprayed in the form of the chloride on the suitably prepared mass. Mention may also be made of pumice, glass wool, silica fibres, fibrox, various porous siliceous materials such as fireclay, alundum, unglazed porcelain, kieselguhr either in powder form or bonded into brick, charcoal, various porous oxides and anhydrous salts. It is interesting to record metallic aluminium as the most recent of catalyst support materials, now being employed as a support for metallic oxides in the air oxidation of hydrocarbons[6] and in the catalytic conversion of acetic acid to acetone,[7] using lime as catalyst. The metal support facilitates thermal equilibrium in the catalyst system. It is employed in a granular form, obtained by allowing the molten metal to cool slowly in trays, the mass, meanwhile, being vigorously shaken.

Theories of Catalytic Action.—For catalysis in homogeneous systems the intermediate compound theory appears to be generally applicable. The activity of water vapor in gas reactions may be attributed generally to a cycle of changes into which the water molecule enters and in which it is finally regenerated. In the lead chamber process of sulphuric acid manufacture a cycle of reactions is postulated for the oxides of nitrogen employed as catalyst. It must be observed that even in such media the possibility of heterogeneity cannot be totally excluded. Water vapor is frequently assumed to act as nucleus in such changes. Williamson's explanation of the function of sulphuric acid in the etherification of alcohol, in which ethyl hydrogen sulphate is an intermediate stage, was the first formulation of the intermediate compound theory in homogeneous liquid systems. It is now generally assumed that most homogeneous catalytic reactions occur thus by stages, and stoicheiometric relationships between reactants and catalysts can normally be postulated in such cases.

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[6] The Barrett Co., Edgewater, N. J.

[7] Stockholms Superfosfat Aktiebolaget, Br. Pat., 1921.

Whilst the intermediate compound theory gives the mechanism by which the reactions occur, it gives no indication at all as to why such successive reactions occur with enhanced rapidity. The radiation theory of chemical action, whereby the necessary energy of reaction is assumed to be absorbed from the thermal radiation of the system in quanta of definite frequency or frequencies, has been recently applied not only to ordinary thermal reactions, but has also been extended to such homogeneous catalytic reactions.[8] One of the recent experimental contributions to this theory has been obtained by H. A. Taylor in Liverpool, England, with reference to the influence of solvent on the reaction velocity. It has been shown that the critical increment of energy, as deduced from the temperature coefficient of reaction velocity, required for the decomposition of triethyl sulphine bromide in nitrobenzene solution, corresponds to a radiation frequency 3.0×10.4 or a wave-length of 1.0μ. Experimental measurement of the infra-red absorption of the bromide in nitrobenzene shows a distinct bend at 1.05μ in good agreement with the theory. Other measurements with other solvents give further support to the observation that the source of necessary energy is the temperature radiation of the system, communicated in terms of a single quantum corresponding to a given frequency or in terms of a small number of quanta of correspondingly lower frequency. The experiments of Daniels and Johnston[9] unquestionably lead to the conclusion that the absorption of energy may occur by means of several quanta as opposed to a single quantum.

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[8] See Lewis, *Journ. Chem. Soc.*, 1914-1920; *Trans. Farad. Soc.*, Sept., 1921.

[9] *Journ. Amer. Chem. Soc.*, 43, 72 (1921).

Attempts have been made to prove the influence of infra-red radiation as an accelerator of reaction by Rideal and Hawkins [10] and by Nil Ratan Dhar.[11] In the former case, experimental error alone will account for all the observed effects of infra-red radiation. The claims of Dhar with reference to sucrose solutions have been negatived by experiments in the Princeton laboratories, as well as by experiments of Lindemann and Taylor in Oxford.[12] It has been shown also by Taylor,[13] and by Lewis and McKeown,[14] that the net result of photochemical infra-red radiation of a solution in bulk must be very small, owing to the high *extinction* coefficient of such solutions for infra-red radiation. The thickness of radiated solution is in most cases confined to a small fraction of a millimetre. Further work in this field should be directed to gas reactions.

For heterogeneous catalytic reactions, the adsorption theory of catalysis has recently received extended experimental test, so that a much clearer picture of reaction processes is now obtainable. Faraday postulated adsorption of hydrogen and oxygen at the surface of a platinum plate to account for the velocity of reaction between these gases at such a surface. The kinetic studies of Bodenstein and his co-workers led Bodenstein and Fink to assume that rate of reaction was determined in many cases by the rate at which the reacting gases could penetrate through a layer of adsorbed gas to the active surface. In this way, the retarding effect of sulphur trioxide on the combination of sulphur dioxide and oxygen at a platinum surface was explained. Langmuir's studies of the reactions of gas molecules at low pressures in contact with metallic filaments, and his studies of oil films on water surfaces, have indicated the existence in such cases of stable adsorbed films, monomolecular in extent, with the molecules oriented on the surface in definite manner. The relative stabilities of such monomolecular layers on the given surface are shown by Langmuir to determine the form of reaction equations obtained in such surface reactions.

The specificity of catalytic agents in respect to adsorption of gases is well illustrated by the measurements of Taylor, Burns and Gauger in experiments with hydrogenation catalysts. Nickel, the most important of such agents, shows marked adsorptive capacity for hydrogen, carbon monoxide and ethylene. Copper, on the other hand, adsorbs carbon monoxide and ethylene to a more pronounced degree than hydrogen, though this latter is measurably adsorbed. As was pointed out, however, by Taylor and Burns,[15] the variation in adsorptive capacity of the agents is alone insufficient to account for the variation in catalytic activity. All of the metals listed in the subjoined table show measurable adsorptions of the reacting gases in the reactions listed. They display, however, the marked divergencies, as catalysts, which are noted in the table.

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[10] *Journ. Chem. Soc.*, 117, 1288 (1920).

[11] *Zt. Anorg. u. Allgem. Chem.*, 1921.

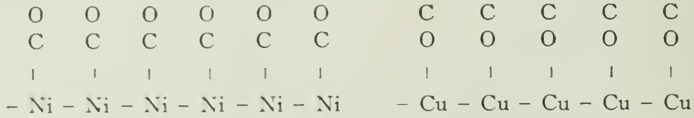
[12] *Nature*, 1921.

[13] *J. Ind. Eng. Chem.*, 13, 75 (1921).

[14] *J. Amer. Chem. Soc.*, 43, 1288 (1921).

Reaction	Catalysts	Non-catalytic
$CO + 3H_2 = CH_4 + H_2O$	Ni, Co, Fe, Pd.	Cu, Pt.
$2CO = CO_2 + C$	Ni, Co, Fe.	Cu, Pt.
$C_6H_6 + 3H_2 = C_6H_{12}$	Ni.	Cu.

It is possible in many such cases that orientation of the adsorbed molecules may be shown to account for such specificity. The orientations postulated in the appended examples might be adduced to account for the activity of nickel and the non-activity of copper in the decomposition of carbon monoxide to carbon dioxide and carbon.



$$\begin{array}{cccccc} \mathrm{O} & \mathrm{O} & \mathrm{O} & \mathrm{O} & \mathrm{O} & \mathrm{O} \\ \mathrm{C} & \mathrm{C} & \mathrm{C} & \mathrm{C} & \mathrm{C} & \mathrm{C} \\ | & | & | & | & | & | \\ -\mathrm{Ni}- & \mathrm{Ni}- & \mathrm{Ni}- & \mathrm{Ni}- & \mathrm{Ni}- & \mathrm{Ni} \end{array} \qquad \begin{array}{ccccc} \mathrm{C} & \mathrm{C} & \mathrm{C} & \mathrm{C} & \mathrm{C} \\ \mathrm{O} & \mathrm{O} & \mathrm{O} & \mathrm{O} & \mathrm{O} \\ | & | & | & | & | \\ -\mathrm{Cu}- & \mathrm{Cu}- & \mathrm{Cu}- & \mathrm{Cu}- & \mathrm{Cu} \end{array}$$

It must be pointed out that such postulates entirely lack experimental confirmation, and, indeed, the idea of a CO molecule, attached to copper and to platinum by the oxygen molecule, is in disagreement with the views expressed by Langmuir[16] in this regard as a result of his studies of the interaction of carbon monoxide and oxygen in presence of platinum.

Orientation of the molecules of dissolved substances at charcoal surfaces is held by Kruyt and Van Duins[17] to account for the variability in the action of charcoal suspended in various liquid systems. Both methyl acetate and sodium hydroxide are adsorbed from aqueous solution by charcoal. No acceleration of reaction velocity is thereby obtained. On the contrary, a retardation results. Charcoal, however, accelerates the interaction of potassium iodide and β dibropropionic acid, because, in agreement with surface tension measurements, the reactive groupings of these substances are brought into close contact on the charcoal surface.

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[15] *Loc. cit.*

[16] *Trans. Faraday Soc.*, Sept., 1921.

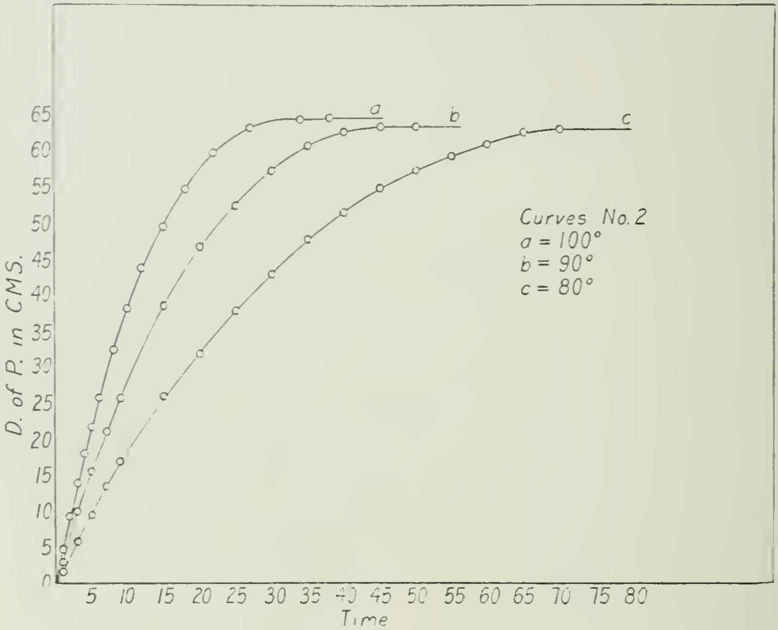
[17] *Rec. Trav. Chim.*. [4]. 2, 249 (1921).

Convincing proof of the divergence between the adsorption of gases by metallic catalysts and by porous inert adsorbents has been obtained by Taylor and Gauger in a study of the adsorption isotherms of hydrogen on catalytic nickel. The experimental data are also in good agreement with Langmuir's view that such adsorption layers are seldom more than monomolecular and are determined in many cases by electronic rearrangements of adsorbent and adsorbed gas. A study of the adsorption isotherms of hydrogen on catalytic nickel at temperatures between 25° C. and 305° C. has shown that nickel is saturated with hydrogen at relatively low gas pressures. Already at 40-mm. pressure at 25° C., nickel is completely saturated with hydrogen and with increase of pressure up to 760 mm. the extent of adsorption does not sensibly alter. At 305° C. it only requires a pressure of 275 mm. to saturate the nickel surface completely with hydrogen, beyond which pressure no further adsorption occurs.

Furthermore, if the minimum pressures, beyond which further increase of pressure does not produce additional adsorption, be regarded as the saturation pressures of a surface nickel-hydrogen complex at the several temperatures, an interesting conclusion may be drawn. It is found that the logarithms of such "saturation pressures" plotted against the reciprocal of the absolute temperatures yield a straight-line relationship, as would vapor pressures or dissociation pressures under similar treatment. From the slope of this straight line it is possible to determine the magnitude of the thermal quantity involved in the disruption, and, therefore, in the formation, of such a surface complex. In the case of nickel and hydrogen under consideration this has been shown to be of the order of 2500 calories per mol of hydrogen adsorbed. An alternative experimental check on this magnitude is now being sought, since another, though less certain, method used by Rideal [18] to determine this magnitude gives a value of 12,000 calories.

The significance of such adsorption isotherms in the problem of reaction kinetics at a catalyst surface may also be emphasized.

FIG. 2.



It is obvious that, if reaction occurs only with measurable velocity at the catalyst surface and in proportion to the concentrations of the reacting gases at such surfaces, the equation will be dependent upon the nature of the adsorption isotherms of the reacting gases. For example, in the reaction yielding hexahydrobenzene,

$$C_6H_6 + 3H_2 = C_6H_{12}$$

the ordinary stoicheiometric equation would require the reaction to be proportional to the cube of the partial pressure of the hydrogen gas. Since, however, the concentration of hydrogen at a nickel surface is independent of the hydrogen gas pressure over a considerable range of pressure (above 100 mm. at 100° C.) it might be anticipated that in the catalytic hydrogenation of benzene the partial pressure of the hydrogen above 100 mm. would have little or no influence on the rate of reaction, provided always that the other gases and vapors present in no way seriously modified the hydrogen adsorption. That such is the case is to be inferred from the initial straight-line nature of curves obtained by Taylor and Dougherty in a kinetic study of the above reaction at 80°, 90° and 100° C. It is impossible to obtain such straight-line relationships for the rate of reaction on any theory which assumes that the hydrogen is acting in proportion of the cube of its partial pressure.

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[18] *Jour. Chem. Soc.*, 121, 309 (1922).

More recent work on the hydrogenation of ethylene in presence of metallic copper by Dr. R. N. Pease, at Princeton, shows, however, that the simple theory, based on adsorption measurements of the single gases at various partial pressures, is not adequate in all cases for the deduction of the kinetics of a reaction in the presence of a catalyst medium. The modifying effects of the other gases present may alter the conclusions. For this reason, adsorptions by a catalyst from mixed gases deserve thorough study.

An interesting phase of the general subject of catalysis is that of preferential catalysis. It is possible, by suitable choice of a catalytic agent, to secure the preferential progress of a given gas reaction in presence of other gases which are also capable of undergoing the same reaction. A familiar example is the preferential oxidation of hydrogen sulphide to sulphur and water

$$2H_2S + O_2 = 2H_2O + 2S$$

in presence of other gases, such as carbon monoxide, hydrogen and methane. This is secured in the purification of illuminating gas by passage of the gas admixed with small quantities of air over a reactive hydrated oxide of iron as, for example, bog iron ore at ordinary temperatures. Another important example of recent industrial development, is the Harger-Terry process of preferential combustion of carbon monoxide with oxygen in presence of hydrogen, a process which has now been applied to the elimination of small quantities of carbon monoxide from hydrogen prepared by the steam-iron process.

A study of the mechanism of this process of preferential combustion from the standpoint of adsorption has recently been made at Princeton by Dr. A. F. Benton. The normal agencies for such preferential catalysis are certain metallic oxides, preferably obtained by precipitation of the hydroxides and low temperature removal of the water. Among the more important of such oxides are those of copper, iron, manganese and cobalt. Experimental test has shown, in all such cases, that the oxides adsorb carbon monoxide to a very considerably greater extent than they adsorb hydrogen, which, in most cases, is only taken up by such oxides to a negligible extent. It is clear, therefore, why, even when the carbon monoxide is present in small percentages in hydrogen, its reaction at the oxide surface preponderates over that of the hydrogen gas.

A detailed study of the kinetics of such combustion processes at the surface of these oxides on their reduction products has indicated the diversity of the problems involved in such catalytic study. The mechanism of catalysis in the case of hydrogen and oxygen on the one hand, and of carbon monoxide and oxygen on the other hand, may be totally distinct. This is clearly demonstrated in work carried out in collaboration with Dr. R. N. Pease and Dr. H. A. Jones. In contact with copper oxide the measurements indicate that catalysis is determined in each case by alternate reduction and oxidation. In presence of reduced copper, the combination of hydrogen and oxygen is apparently also dependent on alternate oxidation and reduction. With metallic nickel this is certainly not the case. Reaction at nickel surfaces is apparently the oxidation of hydrogen adsorbed on the nickel, a reaction which occurs freely, in presence of an active catalyst, at room temperatures. With carbon monoxide and oxygen in presence of reduced copper, the reaction is similar to that with hydrogen and oxygen in contact with nickel and in marked contrast to that obtaining with these latter gases and copper. The mechanism is certainly not an alternate oxidation and reduction but an oxidation of adsorbed carbon monoxide by oxygen, in agreement with the high adsorptive capacity of copper for carbon monoxide and its low capacity for both hydrogen and oxygen. With suitably prepared copper, carbon monoxide and oxygen will react rapidly at 0° C.

Reactions at Boundaries of Phases and the Problem of Promoter Action.—A study of the reduction of copper oxide by hydrogen[19] and by carbon monoxide at moderate temperatures (100–150° C.) has demonstrated the importance of the interface between two phases and the chemical activity which may be located at such points. It has been shown that low temperature reduction of copper oxide by hydrogen or carbon monoxide is negligible until copper nuclei are established in the copper oxide mass. Subsequent reaction is then confined to the boundaries between the copper and copper oxide as can be demonstrated visually by the ever-increasing area of the red copper extending outwards from the original nuclei. The amounts of water vapor and carbon dioxide produced per unit of time as a result of such reduction processes increase steadily with increasing extent of interface; they attain a maximum and then steadily diminish as the reduction of the oxide is completed. The form of such a time-reaction curve is typical of an autocatalytic process. It evidently finds its explanation in the higher order of reactivity of an oxide ion when situated adjacent to a neutral copper atom which is also capable of adsorbing hydrogen, probably in the atomic condition, and also carbon monoxide.

This example of activity at an interface is another case of a variety of such phenomena recently indicated by Langmuir.[20] Faraday observed that a perfect crystal of sodium carbonate or sodium sulphate refuses to effloresce until the surface is scratched or broken and that the efflorescence then spreads from the injured place. Prof. G. A. Hulett has frequently drawn the writer's attention to the similar behavior of hydrated cadmium sulphate which is readily obtained in large and perfect crystals, which maintain a constant weight in a desiccated space until a boundary between a hydrated and a dehydrated phase is established. Langmuir has similarly shown that in the dissociation of calcium carbonate by heat, the carbon dioxide is produced only at the boundary between the calcium carbonate and the calcium oxide phases. The dissociation of silver oxide to yield oxygen and silver, studied by G. N. Lewis,[21] is a parallel case, it being observed that the rate of dissociation increased with increasing production of silver. Silver was termed the autocatalyst of the reaction. Undoubtedly the presence of neutral silver atoms with their free electrons affects the stability of the adjacent oxide ion. Lewis demonstrated the analogy existing between the silver oxide decomposition and the growth of crystals in a saturated solution in which, as is now well known, forces electronic in nature are involved. The different nature of the dissociation process when such interfaces are not set up is well illustrated in the case of mercuric oxide dissociation studied by Hulett and G. B. Taylor.[22] In this case at temperatures where dissociation becomes marked (500° C.), the mercury formed is also vaporized. No interface results and so no acceleration of the dissociation is obtained. As a result, passage of nitrogen gas for twenty-four hours over pure mercuric oxide at 500° C. gave concentrations of oxygen corresponding to only a few mm. pressure, whereas the true equilibrium pressure at that temperature was upwards of one atmosphere. When interfaces were produced by the addition of foreign substances, iron oxide, manganese dioxide and platinum, true equilibrium pressures were at once established, measurable both statically and dynamically. The recent researches of Kendall and Fuchs[23] on the accelerated decomposition of silver oxide, mercuric oxide and barium peroxide in presence of other oxides is also illustrative of the effect produced by the deliberate creation of interfaces. The view expressed by Kendall and Fuchs that the added oxide influences also the dissociation pressure of the oxide has not, in the view of the writer, been unequivocally demonstrated. That the rate of decomposition is accelerated is, however, unquestionable.

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[19] Pease and Taylor, *J. Amer. Chem. Soc.*, **43**, 2179 (1921).

[20] *Trans. Farad. Soc.*, Sept., 1921, *Jour. Amer. Chem. Soc.*, **38**, 2263 (1916).

[21] *Zt. Phys. Chem.*, **52**, 310 (1905).

Enhanced activity at an interface is certainly more common than even the examples already given would indicate. A search of the literature is constantly yielding fresh material in which experiment shows abundant evidence of such interface phenomena manifested as an apparently autocatalytic action. Thus, in a determination of the dissociation pressure of sodium bicarbonate Lescouer[24] observed that the development of pressure occurs "slowly at first, then more quickly towards the end. . . . It has seemed to me, moreover, that the final equilibrium was obtained more rapidly the more the proportion of dissociated salt increased." Experiments undertaken in the Princeton laboratories on the dissociation of ammonium meta-vanadate, which yields a colored oxide, thereby facilitating visual control of the nature of the dissociation process, has given qualitative evidence of the interface phenomenon. The ready decomposition of the finely crystalline salt has prevented decisive proof of this possibility.

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[22] *Jour. Phys. Chem.*, 17, 567 (1913).

[23] *J. Amer. Chem. Soc.*, 43, 2017 (1921).

[24] *Ann. Chim. Phys.*, (6), 25, 430 (1892).

As regards interaction between a solid and a gas, the case of copper oxide reduction by hydrogen and by carbon monoxide, may now be supplemented by the cases of nickel oxide and vanadium pentoxide. These oxides, when reduced at low temperatures, show the phenomenon of auto-acceleration, and in the latter case the interface is rendered visible by the change from a red-brown to a blue-black oxide. Dr. R. M. Burns reports the same feature in the reduction of vanadium pentoxide in benzene-air mixtures. It is anticipated that this list of oxides could be greatly extended.

Langmuir[25] has pointed out that the hydration of a completely dehydrated substance should show the same auto-acceleration. An observation recently made independently by several workers in the Princeton laboratories seems to verify this conclusion experimentally. The dehydration of ethyl alcohol was undertaken with the aid of lime, which test showed to be "over burnt." For two days the lumps of lime remained intact in the alcohol. On the third day a small amount of powder appeared alongside the lumps of lime, while treatment for an additional twenty-four hours resulted in the complete disintegration of the whole of the lime lumps. Qualitatively, at least, this is in accord with the idea of interface activity.

Now the reactivity conferred on a molecule by reason of the proximity of a molecule of decomposition product can also be secured by admixture of the reacting species with a suitable foreign substance. The conclusions of Hulett and Taylor and of Kendall and Fuchs have already been cited in this regard. Doubtless it is oftentimes this effect which accounts for the enhanced activity of a catalytic agent when admixed with small amounts of a suitable foreign substance. Such admixtures are termed catalyst "promoters" and their utilization in technical catalysis is a growing development of the catalytic art, as the appended table of examples will show. A summary of the principal examples of promoter action has already been compiled by Pease and

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[25] *J. Amer. Chem. Soc.*, 387, 2263-2267, (1916).

Taylor.[26] The mechanism of promoter action has received but little study. It is apparent, however, that a suggestive list of

Reaction	Catalyst	Promoters employed or suggested
Contact sulphuric acid process	Burnt pyrites	Oxides of Cu, V, Ur, Cr, Ni, Co, Al, Be, Zr, Zn, Ce, Th and Di
Ammonia oxidation	Oxide of iron	Oxides of Cu, Ca, Bi, Ce, and Cr
	Platinum	Oxides of Pb and Te
Deacon chlorine process	Cuprous chloride	Chlorides of several elements
Removal of sulphur compounds from gases	Iron oxide	Oxides of Cr, Ce and Th
Production of formaldehyde	Various metals	Metallic couples
Oxidation of aniline to aniline black	Copper sulphate or Vanadium chloride	p-diamine or p. amidophenol
Oxidation of naphthalene	Mercuric sulphate	Copper sulphate
$CO + H_2O = CO_2 + H_2$	Iron oxide	Oxides of Cr, Ni, Al, Ce, Th, Zn, Pb, Ur, Na, Cu, Ag and Cu metallic couples
$2CO + H_2$ excess $+ O_2$	Iron oxide	Oxides of Cr, Ce, Th, La and Al
$2CO_2 + H_2$ excess $+ O_2$	Copper oxide	Oxides of Ce, Ag and Mn
Hydrogenation of oils	Reduced nickel	Reduced copper, iron
Ammonia synthesis	Reduced iron	Reduced Mo, W, Co, Ni, Ur. Traces of alkalies

experimental investigations can be put forward on the basis of activity at an interface. It can readily be seen that if added substances increase the lability of decomposable oxides and their reducibility, the general level of reactivity of the molecule under such circumstances should be consistently greater than that of the single oxide in absence of such added substances.

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[26] *Journal of Phys. Chem.*, **24**, 241 (1920).

There is a little evidence that adsorptive effects may be magnified at an interface. The reduction of copper oxide by both hydrogen and carbon monoxide is very pronouncedly retarded by the presence of oxygen in the reducing gas. This is most readily interpreted on the assumption that adsorbed oxygen protects the interface from attack by the reducing gas. The adsorption of oxygen by copper oxide and by copper is, however, known to be small, so that it would be necessary to assume increased adsorptive capacity at an interface to account for the protective action observed. Experimental test of such a view could be best carried out by adsorption measurements with suitable mixtures of materials, one of which is known to function as a promoter to the catalytic activity of the other. In a case recently studied by Taylor and Neville, evidence of enhanced reactivity and of adsorption was obtained by admixture of various substances with carbon, as the subjoined table shows:

Catalyst %	Interaction of C and H_2O at 570°. Gas produced. C.c./min.	Interaction of C and CO_2 at 570°. Gas produced. C.c./min.	Adsorption of CO_2 per g. of C. at 445°. C.c.
20% K_2CO_3	25	2.3	4.4
20 .. Na_2CO_3	7.5	1.0	2.0
7.5 Ni	2.6 (final value)	7.7	1.76
20 .. NaCl	1.8	0.24	0.4
No Catalyst	0.9	0.14	0.33

The interpretation thus far given to these results, however, is that the admixed materials freed the charcoal from mixed oxygen complexes and so increased the active surface of the charcoal for both reaction and adsorption.

Catalyst Poisons.—The inhibiting effect of small quantities of foreign bodies on the activity of a catalyst has yielded satisfactorily to investigation. Poisons may be either permanent or transitory. Thus, silicon compounds, present in the ammonia-air mixture used in the oxidation of ammonia in contact with platinum gauze, are oxidized to silica, are deposited in part on the gauze and destroy its activity by covering up the platinum surface. The poisoning is permanent. Hydrogen sulphide and sulphur compounds transform an iron catalyst in ammonia synthesis and a nickel catalyst in hydrogenation processes to the corresponding sulphides whose activity is zero. The effect of the sulphur compounds is cumulative and it is necessary to regenerate a catalyst so poisoned by suitable means. In the case of an iron catalyst poisoned by sulphur, it is necessary to oxidize the sulphide and then regenerate the metal by reduction of the oxide. All cases of permanent poisoning require such a renewal of the contact mass before original activity is regained.

Transitory poisons in gas reactions are most generally to be explained on the basis of preferential adsorption of the poison from the gas mixture, even though this latter is present in only minute quantities. Thus, water vapor is a transitory poison in ammonia synthesis in presence of an iron catalyst. It is probable also that water vapor is the real poison in the case of oxygen and carbon monoxide in ammonia synthesis in presence of iron, since both these gases undergo quantitative transformation, to water vapor and to methane and water vapor respectively, under the conditions of the synthetic process. All these poisons are, however, transitory in their action since, after the removal of the harmful constituent, provided the action has not been too prolonged, the original activity of the catalyst is restored. Water vapor is doubtless tenaciously held by reduced iron even at the working temperature of ammonia synthesis, circa 500° C., and when present in only minimal concentrations. It should be noted that a poison may be both transitory or permanent according to the catalyst used. In the case of ammonia synthesis, using uranium carbide (which changes to nitride) as catalyst, water vapor, oxygen, and carbon monoxide are permanent poisons. They convert the nitride to an irreducible uranium oxide, catalytically inert. It is this factor that has militated against the technical use of the otherwise very excellent uranium compound as a catalyst in ammonia synthesis.

Metallic catalysts are occasionally poisoned by other metals. Lead, mercury and zinc are marked catalyst poisons for platinum in a variety of catalytic actions. Mercury vapor is a powerful catalyst poison to copper and nickel as hydrogenation catalysts.

Systematic investigation of the rôle of the poison in the case of palladium and platinum catalysts has been carried out in the last two years by Maxted.[27] The decrease in activity caused by the poisons, lead, mercury, sulphur, arsenic and zinc, is directly proportional to the concentration of inhibitant from zero concentration up to that producing practically complete inactivity. The occlusive power of palladium for hydrogen varies directly as the amount of sulphur present as inhibitant. The amount of poison (in this case lead) required to reduce the catalytic activity to one-half is very much less than that which reduces the occlusive power to half its original value. This may be explained by the fact that, while occlusion is not confined to the surface, catalysis is a surface phenomenon. With metals showing adsorption without marked occlusion there would doubtless be complete identity between loss of adsorptive power and loss of catalytic activity.

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[27] *Journ, Chem. Soc.*, 1920, 117, 1501; 1921, 119, 225; 1921, 119, 1280.

Young's Modulus and Poisson's Ratio for Spruce. H. CARRINGTON. (*Phil. Mag.*, May, 1922.)—The design of aeroplanes has made it necessary to know more definitely the elastic constants of the timber employed. This investigation presents the results of an extensive series of measurements. The smallest value of the modulus is in the direction perpendicular to the length of the tree and tangential to the annual rings. Across the rings the value of the modulus is perhaps 60 per cent. greater than in the first direction, while along the grain of the wood it is about twenty times as great. Determinations of Poisson's Ratio are given for all six possible combinations of linear extension with lateral contraction.

G. F. S.

The following are abstracted from the Annual Report of the Director of the Department of Terrestrial Magnetism, Carnegie Institution of Washington, for 1921. In May, 1921, there occurred simultaneously considerable disturbances of the earth's magnetism, striking displays of the aurora and strong earth-currents. The last named interfered greatly with telegraphy and the aggregate of phenomena has served to direct attention to the relations of the earth to the sun, because at the time there was also great sun-spot activity. "Telegraph companies have requested observers of sun-spot to keep them informed of notable solar phenomena in the hope that they might take whatever advance steps repeated experiences would show practicable for the prevention of serious interruptions from this source in telegraphic transmission. So, likewise, these organizations and interested persons are soliciting information regarding disturbances of the electric currents continually flowing in the Earth's crust.

"The Earth's magnetic changes are being continually recorded at about fifty stations, which, unfortunately, are not distributed over the Earth with the desired uniformity; the great majority are in Europe and only about 20 per cent. are located in the Southern Hemisphere. But matters are still worse as regards earth-currents, since they are continuously recorded at less than 10 per cent. of the total number of magnetic Observatories."

The non-magnetic vessel *Carnegie* ended its cruise at Washington on November 10, 1921. It and its predecessor, the *Galilee,* have covered a total distance equal to nearly 15 times the circumference of the earth. On land, field work was carried in East Africa and Madagascar and in certain islands in the Pacific. In coöperation with the Government of New Zealand the Department will maintain an observer at the Apia Observatory established by the Germans in 1902. In addition to these activities it is probable that observations are now in progress in Baffin's Land.

Along with the accumulation of data improvement in instruments are made at the Laboratory and the crude material of observation is collated and interpreted with a view to finding an ultimate explanation of the magnetism of the earth.

The United States of America has good reason to be proud of the work done by Dr. L. A. Bauer and by his coadjutors. Not only is the great problem of terrestrial magnetism approaching solution but S. J. Barnett is attacking the underlying cause of general magnetism.

G. F. S.

Tower to Honor Seamen. (*Marine Review,* June, 1922, p. 240.) —A clock and signal tower in the harbor at Montreal has been completed as a memorial to the merchant seamen who lost their lives in the World War. It stands 180 feet above water level at Victoria pier. The clock has four faces, each 12 feet across, and a bell which weighs four tons and is six feet across. The clock will be electrically operated and at noon daily will discharge a bomb of the type in common use on ships.

R.

Width of Hard-surface Roads. (*U. S. Department of Agriculture Press Service, Clip Sheet 209.*)—A minimum width of 18 feet for hard-surface roads is recommended by the Bureau of Public Roads. The maximum width of truck body generally permitted is 8 feet, and 5½ feet is the ordinary clearance width of automobiles. At an average speed of 30 miles an hour it is unreasonable to expect the driver of an automobile to drive with the wheels closer than 1½ feet to the edge of the pavement, says the Bureau. For trucks at an average speed of 15 miles an hour, this distance should not be less than 1¾ feet on account of the great width of the rear wheel. Three feet seems to be a minimum safe clearance between bodies. Inasmuch as a certain amount of truck traffic is to be expected on all main country roads, the minimum width of surface should be 18 feet to provide these clearances when an automobile meets a truck.

Where the frequency with which trucks pass each other becomes a big factor, as in the neighborhood of large cities, the minimum width of pavement should be 20 feet to provide a clearance of 3½ feet and a safe distance of wheels from edge of pavement.

R.

PHYSICS OF THE THREE-ELECTRODE BULB.*

BY

K. T. COMPTON, Ph. D.

Professor of Physics, Princeton University.

INTRODUCTION.

PROBABLY the discovery and use of the three-electrode bulb mark the most important development in the art of wireless communication for, as sender or receiver, it is the "working" part of modern wireless sets. Its invention followed Edison's discovery of the "Edison" or "thermionic" effect, its study by Elster and Geitel, 1882–1890, and by Fleming, 1890–1896, and the development of the theory of the effect by Richardson since 1904. It is interesting to note, in passing, that the thermionic effect was discovered and studied by physicists of the seventeenth century, but the subject was dropped before significant results were obtained—to be revived and put to important use 200 years later.

The Edison effect can easily be demonstrated by wrapping tin-foil around the glass of an incandescent light bulb—taking care not to make contact with the screw base—and connecting a galvanometer in series with a battery between the tin-foil and one of the wires feeding the filament. If the battery is connected so as to make the tin-foil *negative* with respect to the filament, no deflection of the galvanometer is observed. If, however, the tin-foil is *positive,* the galvanometer indicates a current. This current comes as a stream of negative electrons from the hot filament, through the glass to the tin-foil, through the galvanometer and battery and back to the filament. No current flows in the above circuit until the glass inside the tin-foil becomes hot enough to be sufficiently conducting. This experiment may be performed with a tungsten filament lamp, but an old style carbon filament lamp gives a larger current unless the tungsten lamp is run over-voltage.

NATURE OF THERMIONIC EMISSION.

The principal investigations of the emission of electrons from hot bodies have dealt with the effects of the nature of the metal and its temperature on the number of electrons emitted per second and on the velocities with which they are emitted.

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* Presented at a meeting of the Section of Physics and Chemistry of The Franklin Institute, held Thursday, April 13, 1922.

It is found that the electrons emitted from any pure metal at a given temperature emerge from it with all possible velocities between zero and a very high value, probably infinity, and that the relative numbers with various velocities are distributed according to Maxwell's probability law, with an average velocity which is proportional to the absolute temperature of the metal. In other words, the relative numbers with different velocities are the same as if the electrons were molecules of an ideal gas. It was first thought [1] that these velocities were the same as if the electrons were molecules of an ideal gas *at the temperature of the emitting metal,* but recent investigation has shown that their average kinetic energy is about twice this large, as if characteristic of about *twice the temperature of the metal.* An idea of the distribution of velocities among the emitted electrons may be gained from Table I, in which the velocities are expressed in terms of the equivalent number of volts V from the relation $\frac{1}{2} m v^2 = \frac{eV}{300}$.[2] The last column gives the fraction of all emitted electrons whose velocities

Table I.

Energy of Emission less than	at 1050° K. (volts)	at 3150° K. (volts)	Fraction
$\bar{V}$	0.27	0.80	0.392
$2\bar{V}$	0.54	1.60	0.112
$3\bar{V}$	0.80	2.40	0.032
$4\bar{V}$	1.07	3.20	0.0086
$5\bar{V}$	1.34	4.00	0.0019
$6\bar{V}$	1.60	4.80	0.00042
$7\bar{V}$	1.87	5.60	0.00011
$8\bar{V}$	2.14	6.40	0.000027
$9\bar{V}$	2.40	7.20	0.0000060
$10\bar{V}$	2.67	8.00	0.0000014

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[1] Richardson and Brown, *Phil. Mag.,* 93, 1908; Richardson, "Emission of Electricity from Hot Bodies," Chap. V.

[2] e and m are the charge and mass of an electron and 300 is a factor to convert from electrostatic units of potential to volts. V is the number of volts of potential drop in which an electron would acquire a velocity v. $\bar{V}$ is the average energy, in volts.

exceed the value indicated in the other columns. For instance, at 1050° absolute, 0.0019 of the emitted electrons have energies exceeding five times the average energy, or possess sufficient kinetic energy to pass against a retarding field of 1.34 volts.

This type of velocity distribution is similar to that among the molecules of a vapor which have just escaped by evaporation from a liquid surface. It suggests that thermionic emission is really an evaporation of electrons from the surface of the hot metal.

Richardson first applied this conception to the theory of thermionic emission. Within the metal there are electrons with velocities distributed as if they are molecules of an ideal gas. Those which strike the surface will escape if their kinetic energy exceeds the work which they must do against the retaining forces at the surface. These retaining forces include the attraction exerted on the escaping electron by the positive charge induced by it on the surface, and the total work done against these forces is the "heat of evaporation" of the electrons. This work is often called the "work function" and written as $e\phi$, where ϕ is the equivalent potential difference. On this theory, Richardson showed that the thermionic current per square centimetre of emitting surface should be

$$i = N e \sqrt{\frac{k}{2 \pi m}}\, T^{\frac{1}{2}} \, \epsilon^{-\frac{e \phi}{k T}}, \tag{1}$$

where N is the number of free electrons per unit volume in the metal, k is the Boltzmann gas constant in $pv = nkT$, and T is the absolute temperature.

The same theory, applied to the Thomson effect in metals, indicates that N is closely proportional to $T^{\frac{3}{2}}$ so that the true variation of thermionic current with temperature should be given by the equation

$$i = A\, T^2 \, \epsilon^{-\frac{e \phi}{k\, T}}, \tag{2}$$

in which A is a constant. The same equation was derived by Richardson on more general grounds, without postulating the existence of free electrons within the metal, and Dushman[3] has recently given grounds for supposing that A has the same value for all metals, and has calculated its value. Thus the thermionic properties of metals seem to be determined entirely by the temperature T and the work function, or "latent heat of evaporation of an electron," ϕ. To obtain large thermionic currents it is necessary to use a substance with a small value of ϕ and with a high enough melting point to permit its use at a high temperature.

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[3] Paper at Washington Meeting of American Physical Society, April, 1922.

Equation 2 has been tested over an enormous range, with sufficient temperature variation to produce a variation of ten million million fold, or 10^{13} fold, in the thermionic current, without detecting any inaccuracy in equation 2.[4] Table II gives some actual currents from a tungsten wire. Currents as large as 8 amperes per square centimetre of emitting surface have been obtained. A convenient method of testing equation 2 is illustrated by Fig. 1, in which the equation is plotted in its logarithmic form. In this form, the graph of the observed values of i and T should give a straight line, such as BC.

Table II.

Temperature	Thermionic Current	
1050°K.	0.000000235	microamps.
1200	0.000169	per sq. cm.
1350	0.0282	
1500	1.70	
1650	49.0	
1800	809.	
1950	8730.	
2100	67000.	
2250	394000.	etc.

THE "WORK FUNCTION" ϕ.

The slope of the curve, as plotted in Fig. 1, gives the value of the work function ϕ characteristic of the metal from which the plotted values were obtained. This value, and the intercept $\overline{OA}$, determine the other constant A.

Since the work function ϕ is of the nature of a heat of evaporation, we should expect a metal to be cooled by its thermionic emission just as a liquid is cooled by evaporation. This was found by Cooke and Richardson[5] to be the case. They used a metal filament as one arm of a sensitive Wheatstone's bridge, which provided its heating current and measured its resistance. The filament was surrounded by a coaxial electrode which could be charged negatively or positively with respect to the filament so as to prevent or permit the emission of a thermionic current from the filament. When this emission was permitted, the temperature of the filament was observed to decrease. From the additional amount of energy of heating current required to bring the filament back to its original temperature, the total rate of loss of heat by evaporation of electrons was determined. From this the heat of evaporation per electron, ϕ, was calculated and found to agree with the value obtained as in Fig. 1.

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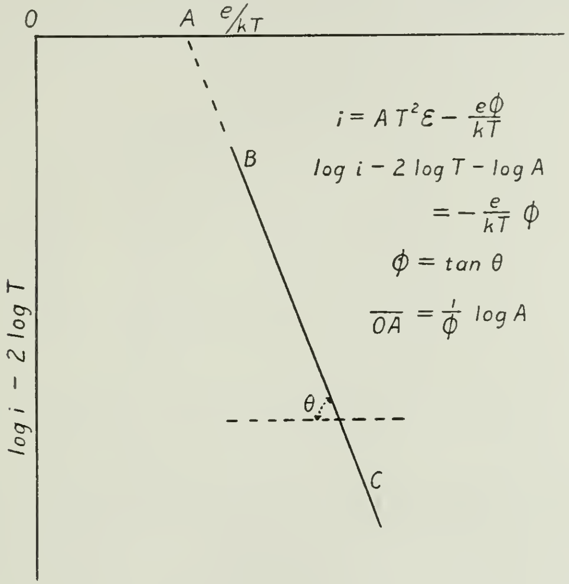
[4] K. K. Smith, *Phil. Mag.*, 1915.

[5] *Phil. Mag.*, **20**, p. 173, 1910; **25**, p. 624, 1913.

FIG. 1.



A third method of measuring ϕ is to consider it as a "heat of condensation." That is, heat should be developed in a metal when electrons pass into it through its surface. This was also proved and ϕ measured by Richardson and Cooke,[6] who observed the increase in temperature of a thin metal strip, which formed one arm of a Wheatstone's bridge, when electrons passed into it from a neighboring hot filament.

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[6] *Phil. Mag.*, 20, p. 173, 1910; 21, p. 404, 1911.

Finally, there is a relation between the values of ϕ and the contact difference of potential of metals which is useful in estimating or predicting values of ϕ for metals which have not been accurately investigated by the preceding methods. Consider two metals (1) and (2), connected at the junction J and placed in an enclosure at constant temperature. Calculate the work done in the processes involved in taking an electron around a cycle as follows: Starting in (1), take it out through the surface of the metal, doing work $e\phi_1$ on it. Then take it to a point just outside the surface of (2), doing work $e(V_2 - V_1)$ against the contact difference of potential between the metals. Then take it through the surface into (2), in which process it does work $e\phi_2$. Finally, take it around through the metals, across the junction J to the starting point, doing work at the junction equal to eP, where P is the Peltier coefficient for the metals. The work done against metallic resistance may be neglected, since this depends on the square of the current and we may imagine the process to be performed as slowly as we please. The total work done must be zero, since it is a reversible cycle at constant temperature. Therefore,

Table III.

Metal	ϕ (in volts)
Pt	5.3
W	4.4
Mo	4.04
Ca	3.04
Na	2.65
BaO	3.65
CaO	3.48

$$V_1 - V_2 = \phi_1 - \phi_2 + P. \tag{3}$$

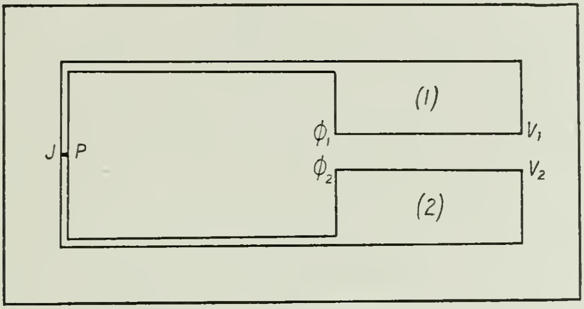
P is so small as to be practically negligible, whence we see that the difference between the work functions of two metals equals their contact difference of potential. A very electropositive metal has a small value of ϕ. Equation 3 has been verified by direct experiment with only moderate accuracy, since the values of V are very difficult to determine free from spurious effects. Indirect verification of the equation has, however, been quite convincing.

Table III gives a few typical values of ϕ. Expressed in equivalent volts, the average kinetic energy of a gas molecule is 0.13 volt at 1000° K., 1.3 volts at 10,000° K., and 6.5 volts at

50,000° K. We see that ordinary temperatures are sufficiently low to keep electrons from rushing freely out of metals, only a minute fraction of them having sufficient energy to escape.

It is desirable, in a three-electrode bulb, that the thermionic emission from the filament be large, homogeneous as regards velocity distribution, obtained with a minimum expenditure of battery power, and absolutely constant under constant external conditions. Large currents are obtained with large area of emitting surface, high temperature and small ϕ. Tungsten is therefore superior to platinum, for it combines a smaller value of ϕ with a much higher melting point. Homogeneity of velocities demands low temperatures, which, in turn, necessitate a substance with a small value of ϕ. For this reason, platinum strips coated with the oxides of the electropositive and fairly non-volatile alkaline earths are advantageous. These are also advantageous because of their operation with minimum expenditure of battery power, since they give good emission at a dull red heat, whereas tungsten must be heated to bright incandescence. Pure metals are probably preferable to oxide coated filaments as regards constancy, although the constancy of the present commercial bulbs with oxide-coated filaments is remarkable.

FIG. 2.



$$V_1 - V_2 = \phi_1 - \phi_2 + P$$

A very recent development which may be important was reported by Langmuir.[7] Thoriated tungsten filaments, given proper heat treatment, become coated with a surface layer of thorium which is very stable unless the temperature is excessive. The filament then has the properties of a thorium filament and combines very advantageously a relatively low value of ϕ with ability to operate at a moderately high temperature.

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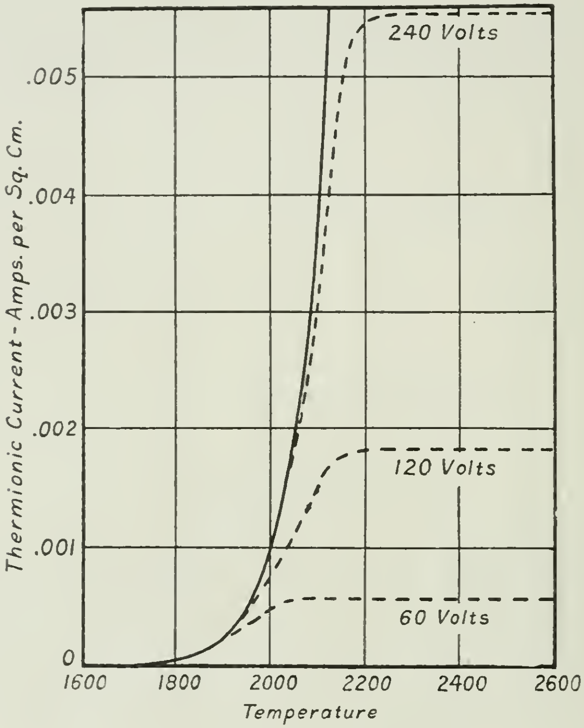
[7] *Proc. Am. Phys. Soc.*, Washington meeting, April, 1922.

If the prime requirement is a maximum emission, nothing equal to tungsten is known.

Fig. 3.



EFFECT OF SPACE CHARGE.

Although equation 2 gives the total rate of emission of electricity from a metallic surface, the actual thermionic current is often less than this because some of the emitted electrons return to the emitting metal, being forced back by the repulsion of other electrons which have been emitted just ahead of them. The region surrounding the emitting metal contains electrons and thus has a "space charge" which tends to prevent the emission of additional electrons. On the other hand, an electric field may be applied to aid the escape of emitted electrons. The current, therefore, adjusts itself to such a value that the accelerating effect of the applied electric field is just balanced by the retarding effect of the space charge, so that the resulting electric field just outside the surface of the metal is zero.

Actually, due to their initial velocities, electrons will be able to escape against a small opposing field, so that the current is really a little larger than that which would just give the balance suggested above. The emitting surface is surrounded by a region of opposing field which reaches zero at a surface of minimum potential at some point outside the metal. Here the field changes direction and is an accelerating field in the remaining interval to the anode.

Fig. 3 illustrates the effect of space charge in limiting the thermionic current. The heavy curve gives the maximum current possible at each temperature and agrees with equation 2. To obtain such currents, a sufficiently large accelerating electric field must be used to completely offset the effect of the space charge. The effect of using smaller accelerating fields is shown by the broken curves, which give experimental results for 60, 120 and 240 volts, respectively. For a low voltage, the experimental curve departs from the theoretical curve at small currents, whereas the curves at higher voltages agree with the theoretical curve to much larger currents. It is seen that, for 60 volts, the maximum possible current is given at 2050° K., and further increase in the temperature of the filament does not increase the current. Similar maximum currents are characteristic of each other voltage.

For a hot filament, the actual current is seen to depend on the applied voltage, as long as the current is less than that given by equation 2. These currents I_{60}, I_{120}, etc., are found to be proportional to the 3/2 power of the corresponding voltages. Langmuir has shown [8] that the above considerations lead to a relation between the current density i and the voltage V, for values of i considerably less than those given by equation 2, of the form

$$i = 2.33\,(10)^{-6}\,d^{-2}\,V^{3/2} \text{ amps. per sq. cm.} \tag{4}$$

if the electrodes are parallel plates distant d apart, and

$$i = 14.65\,(10)^{-6}\,r^{-1}\,V^{3/2} \text{ amps. per sq. cm.} \tag{5}$$

for a small straight filament surrounded by a coaxial cylinder of radius r.

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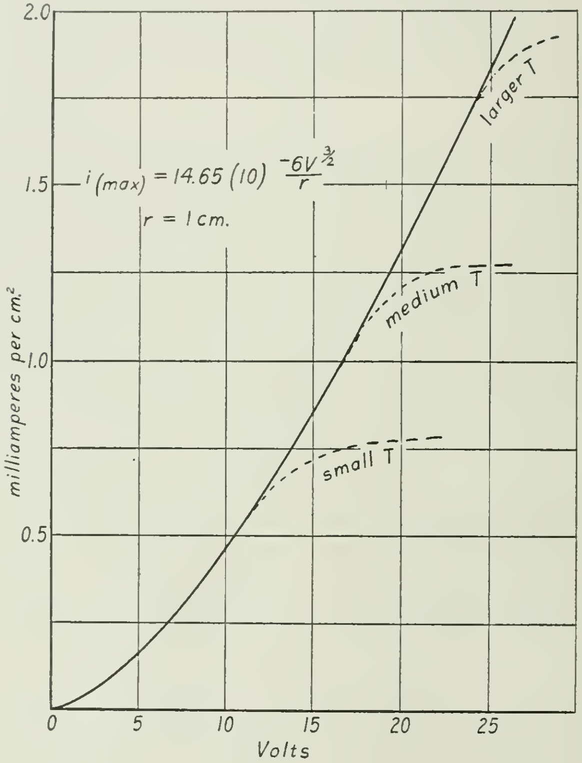
[8] *Phys. Rev.*, 2, p. 450, 1913.

The actual relation between filament current and voltage is shown by Fig. 4, which was calculated for the case of a cylindrical anode of unit radius. The solid curve represents equation 5. At any temperature the currents depart from this curve as the saturation value given for that temperature by equation 2 is approached.

FIG. 4.



Note that for 20 volts, for instance, it is impossible to obtain a current greater than 1.3 m.a., no difference how hot the filament is. But a greater current could be obtained at 20 volts and high temperatures if the distance r between the electrodes were diminished (or, as we shall see later, if positive gas ions are present to neutralize the negative space charge. The above conclusions regarding the effect of space charge apply only to the case of electrodes in a high vacuum).

ELECTRON ATMOSPHERES.

Let me now call attention to a necessary consequence of the facts of thermionic emission, *i.e.*, to the existence of an electron atmosphere at the surface of every metal and extending out with diminishing density to greater distances from its surface. We may picture to ourselves the cause of this atmosphere in the following way. Electrons within the metal continually reach its surface with sufficient kinetic energy to carry them a greater or less distance out, against the attractive forces (which give rise to the work function) which tend to draw them back into the metal. Some few have sufficient energy to escape. The rest are drawn back into the metal, after a short-lived freedom. Thus, at any given distance from the surface, there is a certain average number of electrons per unit volume, or electron density, which remains constant although the particular electrons in this group are continually changing. At higher temperatures this electron atmosphere is denser and extends farther from the surface, owing to the greater kinetic energy of the electrons. Electrons in this atmosphere will collide with each other and behave as molecules of a gas in a field of force.

This force of attraction back toward the metal may arise jointly from several causes, but, unless the atmosphere is very dense, the principal cause is probably the attraction due to the equal positive charge induced by each escaping electron on the surface of the metal. If we assume, as a first approximation, that this is the *only* cause, and that the surface of the metal may be considered as perfectly continuous, instead of being composed of discrete atoms with intervening gaps, we may draw conclusions regarding the electron atmosphere as follows:

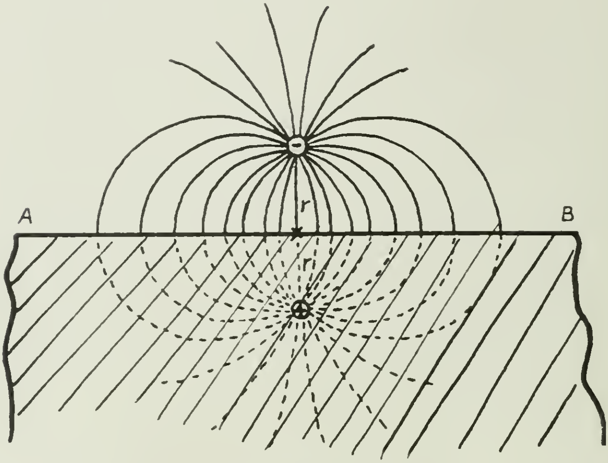
Let AB be the surface of the metal and an electron be distant r from it. The electric field due to the induced positive charge on the surface is the same as if due to the positive "mirror image" of the electron at a depth r within the metal. The force of attraction of the electron toward the surface is, therefore $F = e^2/4r^2$. The work done by an electron which escapes from the surface is thus

$$W = e\phi = \int_a^\infty \frac{e^2}{4r^2}\,dr = \frac{e^2}{4a}, \qquad (6)$$

where a is the distance from which the electron started, so that $2a$ is the initial distance between the electron and its accompanying positive charge.

According to a well-known theorem of statistical mechanics, the numbers of electrons n_1 and n_2 at any two different positions in a field of force depends on the work ${}_2W_1$ required to take an electron from the second to the first position according to the equation

FIG. 5.



$$\frac{n_1}{n_2} = \epsilon^{-\frac{{}_2W_1}{kT}} \tag{7}$$

where ϵ is the base of the Naperian logarithms and T is the absolute temperature. If the second position is the initial position at a distance a, so that $n_2 = n_a$, and if the first position is any position distant r, we have the number of electrons per unit volume at distance r given by equations 7 and 6 as

$$n = n_a \epsilon^{\frac{e^2}{4kT}\left(\frac{1}{r}-\frac{1}{a}\right)}. \tag{8}$$

To determine n_a we notice that the saturation value of the thermionic current, as given by equation 2, must depend on the density n_∞ at relatively great distances $r = \infty$ from the metal in a way which is easily shown by kinetic theory to be

$$i_{\text{max.}} = n_\infty e \sqrt{\frac{k T}{2 \pi m}} . \tag{9}$$

This gives the value of n for $r = \infty$, and hence enables the constant n_a in equation 8 to be determined.

From these equations, I have calculated the electron densities given in Table IV at various distances from the surface for the case of tungsten, $\phi = 4.4$ volts and $i_{\text{max.}} = 8$ amperes per square centimetre at 3000° K., whence $2a = 1.6(10)^{-8}$ cm.

TABLE IV.

d (cm.)	n (300°K.)	n (1000°K.)	n (3000°K.)
$0.8\ (10)^{-8}$	$3.0\ (10)^{20}$	$3.0\ (10)^{20}$	$3.0\ (10)^{20}$
$1.0\ (10)^{-8}$	$1.5\ (10)^{5}$	$7.6\ (10)^{15}$	$8.7\ (10)^{18}$
$2.0\ (10)^{-8}$	$1.9\ (10)^{-26}$	$4.3\ (10)^{6}$	$7.1\ (10)^{15}$
$4.0\ (10)^{-8}$	$7.4\ (10)^{-42}$	$1.0\ (10)^{2}$	$2.1\ (10)^{14}$
$1.0\ (10)^{-7}$	$4.4\ (10)^{-51}$	$2.0\ (10)^{-1}$	$2.5\ (10)^{13}$
$1.0\ (10)^{-6}$	$1.0\ (10)^{-56}$	$3.6\ (10)^{-3}$	$6.8\ (10)^{12}$
∞	$3.0\ (10)^{-57}$	$3.0\ (10)^{-3}$	$5.9\ (10)^{12}$

Evidently the electron atmosphere is extremely rare at appreciable distances from metals at ordinary temperatures. Experimental evidence regarding its detection at ordinary temperatures is conflicting. R. W. Wood[9] reports currents of several milliamperes between optically flat plates of speculum metal, separated by fine quartz fibres, with application of only a few millivolts. On the other hand, Millikan and Shackelford were unable to draw electrons out of gas-free metals with potential gradients lower than about four million volts per centimetre, and suggest that such electron discharges previously reported are due, in some way, to surface impurities.[10] However this may be, the fact of thermionic emission proves the existence of such atmospheres at higher temperatures, and there is no reason for doubting their existence at lower temperatures, although with lower density and extending not so far from the surface.

Recently, in our laboratory, a significant proof of electron atmospheres at high temperatures was obtained. An incandescent tungsten wire was mounted close and parallel to a tungsten strip. The thermal expansion of the leads caused the wire slowly to approach the strip. The ammeter, in series with a battery and the gap between wire and strip, registered the normal thermionic current until the approach was very close, when the current began rapidly to increase with increasing proximity. Before actual contact was made, the thermionic current had risen to many times its normal value. This must have been due to an approach within the region in which the electron atmosphere around the filament showed a noticeable increase in density.

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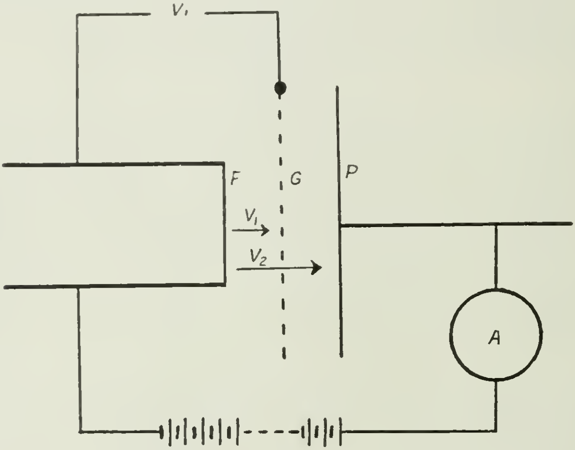
[9] *Phil. Mag.*, 24, 1912.

[10] *Phys. Rev.*, 15, 1920.

FIG. 6.

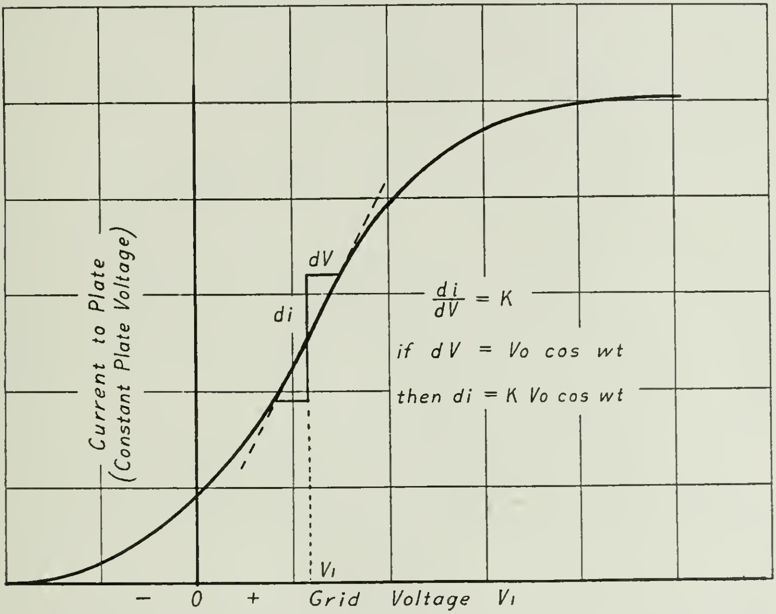


It should be emphasized that the above calculation of densities is necessarily very rough. Actually the metal surface consists of discrete atoms, so that the law of force is more complicated than that underlying equation 6. Furthermore, the effect of the space charge will modify the force on an electron at any point, tending to spread the electron atmosphere to a greater distance from the metal, but with less density near the metal. Nevertheless it is probable that for points not too near the surface, the electron densities are somewhat as given in Table III.

ELECTRIC VALVES.

An electric valve is a device which permits the passage of an electric current in one direction only. It is evident that any combination of two neighboring conductors not in contact, one of which is surrounded by an electron atmosphere, whereas the other is not, constitutes an electric valve. Electrons can pass continually from the one with the atmosphere to the other, but cannot pass in the reverse direction. Now a hot and a cold metal constitute such a combination. The hotter is the hot metal, the greater is the current-carrying capacity of the valve; while the colder is the cold metal, the more perfect is the rectification. The "Kenetron" is an example of this type of thermionic rectifier. I have wondered if the action of crystal rectifiers may not be due to some peculiarity of distribution of electron atmospheres around the surfaces of crystals.

FIG. 7.



THE THREE-ELECTRODE VALVE.

Fig. 6 shows the elements of a three-electrode valve, and their simplest mode of connection. Electrons are emitted thermionically by the filament F and pass toward the perforated grid G if the field V_1 is in the appropriate direction. Since the grid has very large mesh, most of the electrons which reach it pass through the openings and are attracted to the plate P. The ammeter A, or a telephone receiver or other detecting device, is operated by this plate current.

If V_1 is connected to a source of variable electromotive force, the field V_1 varies and consequently the current reaching and passing through the grid will vary. If the thermionic current is large, these variations in the plate current may be very large, even though the current applied to the grid is only large enough to produce the variations in its electrostatic potential, these variations being opposed, to a certain extent, by that portion of the electronic current, which actually reaches the grid instead of passing through. Thus this device is an *amplifier*.

The conditions necessary to secure large amplification and true reproduction of the variable electromotive force applied to the grid are illustrated in Fig. 7. The curve is of the type of Fig. 4. The current at a negative, or retarding, grid voltage is due to the fact that the electrons are emitted from the filament with initial velocities. If the grid is maintained, by a battery through a high resistance, at an average potential V_1, and if a variable electromotive force dV from the antenna is superimposed, then the plate current is varied by an amount di.

To secure maximum amplification, V_1 must be chosen at the point of maximum steepness of the current-voltage curve, *i.e.*, at the point of inflection. If K is the slope of the curve, then

$$di = K\,dV. \qquad (10)$$

Furthermore, for short distances on each side of this point of inflection the slope is practically constant, so that, if the variable e.m.f. to the grid is a simple harmonic function of the time,

$$d\,V = Vo \cos w\,T\,,$$

then (11)

$$d\,i = K\ Vo \cos w\,T\,.$$

Thus the amplified current faithfully reproduces the current which is being amplified. If two-stage amplification is desired, the amplified current from the first-stage tube may be passed through the primary of a step-up transformer, whose secondary is connected to the grid of the second-stage tube.

GAS-FILLED TUBES. DETECTORS.

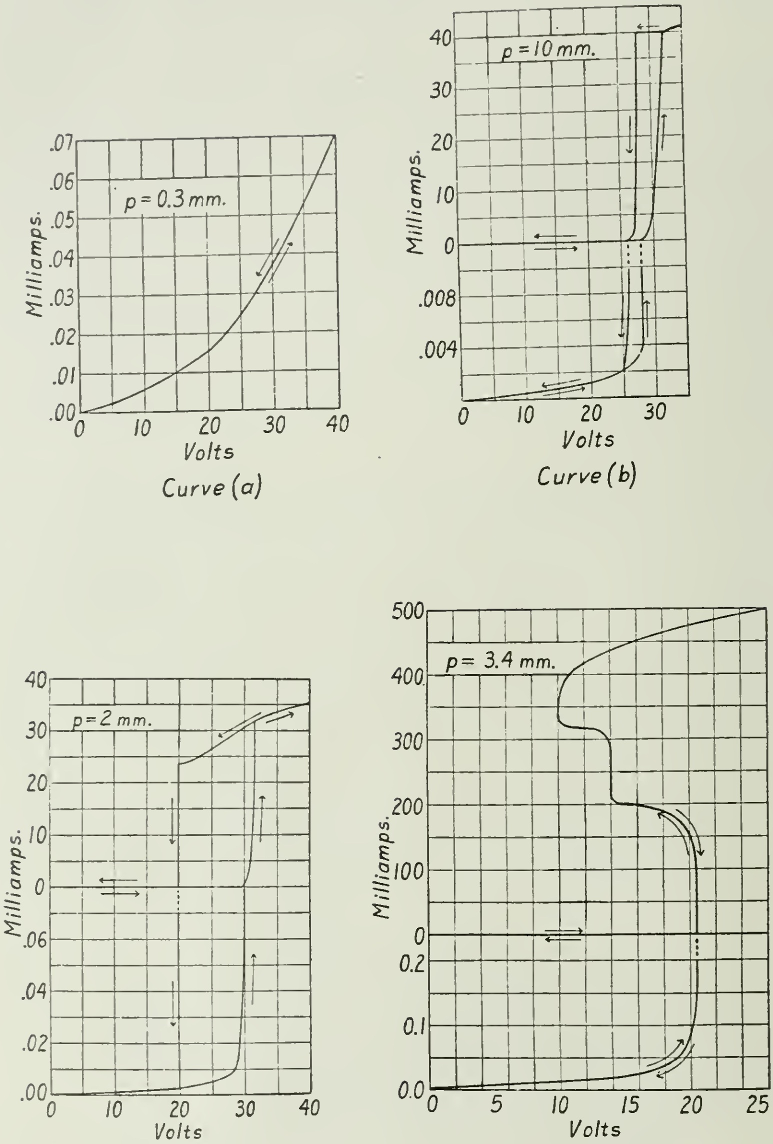
The preceding relations between voltage and thermionic current hold true only when the electrodes are in so good a vacuum that effects of collisions of electrons with gas molecules are negligible. When even a minute amount of gas is present the results are very different. At low voltages the thermionic currents are much reduced by the presence of the gas, owing to the fact that electrons emitted by the filament are likely to collide and therefore escape from the region of negative space charge around the tube less quickly than if the gas were absent. If the gas is multi-atomic, the electrons start practically from rest after each collision, while, if the gas is monatomic, the electrons rebound elastically. The effect of a gas is, therefore, to increase the negative space charge around the filament and therefore to reduce the thermionic current. This decrease is greater in monatomic than in multi-atomic gases, since the zig-zag path of an electron through a monatomic gas causes it to remain longer in the immediate neighborhood of the filament.

If the voltage is high enough to cause electrons to ionize gas molecules, the situation is quite different. The positive gas ions, which are drawn toward the filament, neutralize more or less of the negative space charge around the filament and thus permit the escape of more electrons, some of which produce additional positive ions, and so on. Each positive ion neutralizes the space charge of a large number of electrons, since it remains longer in the region of the space charge because of its greater mass and consequent slower motion. If the amount of ionization in the gas is sufficient to permit, by neutralization of negative space charge, the escape of a number of electrons approaching that for maximum or saturation emission characteristic of the temperature of the filament, then the resultant space charge becomes less negative, with the result that the distribution of potential between the electrodes changes so as to give a greater fraction of the entire potential drop in the immediate neighborhood of the filament. This favors further ionization, with the result that the space charge becomes positive and the total current becomes equal to the saturation thermionic current characteristic of the filament temperature, plus a small additional current due to the gas ions.

These stages in the current-voltage curve, in the presence of a gas, are illustrated by Fig. 8, for the case of a tube filled with helium at the indicated pressures.

Curve (a) is at a pressure and thermionic current density too low to give an arc. Indication of ionization is given by a " break " in the curve at 20 volts. Curve (b) shows an arc pro-

FIG. 8.



Curve (a)

Curve (b)

Curve (c)

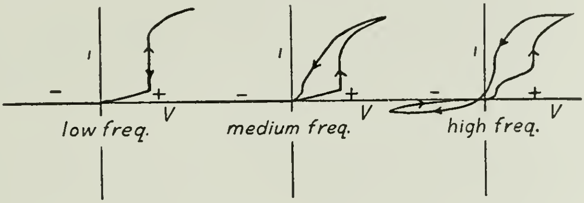
Curve (d)

duced by emission from a relatively cool filament. Not sufficient ionization to produce the arc was obtained until a voltage of

28 volts was applied. With decreasing voltage, however, the arc was maintained at a lower voltage. Curve (c) is a case of a hotter filament, where the arc still strikes at a voltage higher than 20 but breaks definitely at this voltage. With the hottest filaments, the arc both strikes and breaks at the definite minimum of 20 volts, although it may be maintained at a lower voltage, curve (d).

The relative increase in current when the arc strikes may be enormous, amounting to as much as 50,000 fold with scarcely noticeable change in voltage at 20 volts. A two- or three-electrode tube could therefore be used as a *detector* of very great sensitiveness by adjusting the voltage to a value just less than the striking voltage, so that the increased voltage impressed by the incoming signal causes the arc to strike. Almost infinite amplification may be thus secured. Even if the arc is not used, the gas pressure or filament temperature being too low to produce it, very great amplification may be obtained because of the steepness of the current voltage curve beyond the ionizing point.

FIG. 9.



Unfortunately, however, the use of ionized gases to increase amplification is attended with complications which probably render such methods of little value except for very special work. Chief among these difficulties are non-reversibility and lag effects, which produce serious distortion. Fig. 8 illustrates that, except under special conditions, the course of the current-voltage curve depends upon whether the voltage is increasing or decreasing. This is due to a difference in the distribution of potential in the space between the electrodes in the two cases.

Lag effects, as illustrated in Fig. 9, are due to the time required for the recombination of ions and for abnormal, or partially ionized, molecules to return to their normal stable conditions. These curves are approximate reproductions of some very interesting unpublished results obtained by Mr. Kannenstine, at the

University of Chicago. They represent oscillograph records of the variation of the current, due to thermionic emission from a filament in an atmosphere of helium gas, as the voltage between the electrodes is varied. Curve (a) represents a stage intermediate between curves (a) and (b), Fig. 8, when the voltage is varied slowly. Curve (b) is taken under similar conditions with the voltage varied more rapidly, as by a 60-cycle e.m.f. Curve (c) shows the results with an e.m.f. of still higher frequency. In curve (b) on the return curve, some of the helium molecules have persisted in an abnormal state which renders them ionizable at voltages down to about four volts. In curve (c) this effect is more pronounced, since the time is shorter. Not all the ions have recombined or have been drawn to the electrodes in the period of the cycle, as is evident from the reverse current during the negative cycle. And some abnormal molecules are still present when the positive part of the cycle is again reached as is shown by the increased current at about four volts.

Consideration of the operation of a three-electrode bulb, as presented in Fig. 7 and its discussion, makes it evident that gas-filled bulbs with characteristics, as shown in Figs. 8 and 9, will not function satisfactorily as amplifiers for ordinary high-frequency transmission. As detectors, valves, keys, etc., they may be of considerable advantage.

CONCLUSION.

It is evident to you that I have kept closely to my subject, The *Physics* of the Three-electrode Bulb, and have attempted to give a survey, necessarily incomplete, of some of the physical phenomena which have become of great practical importance in their applications and which have also had very important bearing on our ideas regarding the nature and structure of matter and electricity. I have not attempted to discuss details of practical operation of three-electrode bulbs, for two sufficient reasons: Time did not permit discussion of both aspects of the subject, and I am not a practical expert in the use of three-electrode bulbs.

For any who are interested in practical uses of the three-electrode bulb, the following books are suggested: "Radio-Communication," Mills; "Thermionic Vacuum Tube and its Applications," Van der Bijl; "Vacuum Tubes in Wireless Communication," Bucher.

A PRECISION HIGH-SPEED OSCILLOGRAPH CAMERA.*

THE PRECISE MEASUREMENT OF SMALL TIME INTERVALS

BY

E. A. ECKHARDT, Ph. D.

Physicist, Chief of Sound Laboratory, National Bureau of Standards.

In the oscillographs generally used in the electrical laboratories of the United States, the more or less sinusoidal wave of the 60-cycle supply is ordinarily used to provide the time scale. This is generally adequate in investigations involving the frequencies of ordinary power supply. On the other hand, the oscillographic study of the phenomena attending (1) the closing or opening of circuits, (2) fuse protector or circuit-breaker action, (3) dielectric break-down, (4) relay and transformer action, often require a more precise time scale.

A further requirement of many of these problems is an increased film speed. This is necessary to draw out the record so that the details of the recorded event shall not be confused by too close crowding, or in order to obtain the required accuracy of time measurement.

Problems demanding the use of high film speeds and precise time scales have led to the development in our laboratory of a high-speed oscillograph camera, and associated time-scale apparatus which have proven very convenient and effective as tools of research and of measurement and consequently their description here seems worth while.

The character of our laboratory activity made it seem advisable not to design the high-speed camera as an integral part of any one oscillograph, but rather as a complete camera unit with sufficient flexibility to make it available for use with any one of a number of oscillograph types. The variety of combinations in which the camera has already been used has fully justified this feature of the design.

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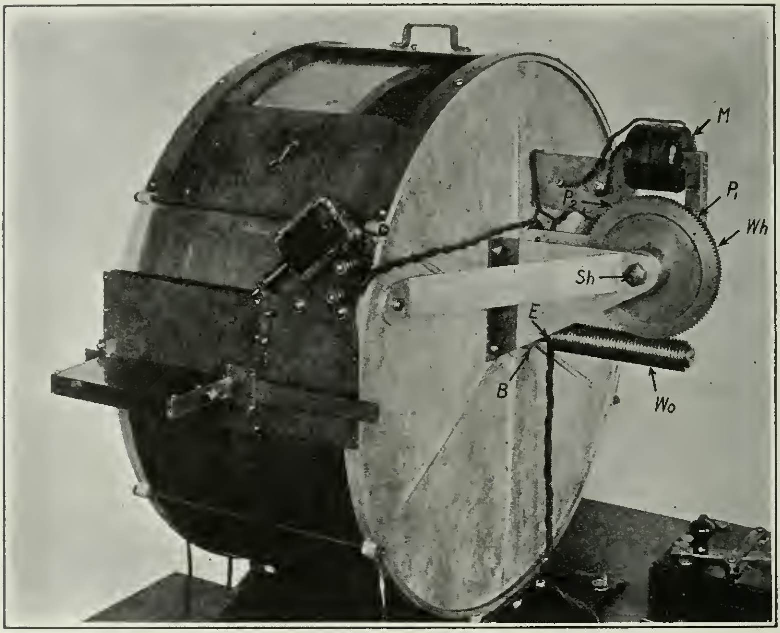
* Presented at a meeting of the Section of Physics and Chemistry of The Franklin Institute held Thursday, December 8, 1921.

If long films are to be used one has the choice of unrolling the film from one small drum on to another during the exposure interval, or of using a single drum of sufficiently large circumference to accommodate the entire length of film. The first alternative involves the starting in motion of the film as the exposure begins. This makes uniform film-speed quite difficult to attain. The large drum, on the other hand, can be brought up to speed prior to the exposure. Conditions are, therefore, favorable for uniform motion of the film at high speeds. The shutter mechanism, however, in this case must operate with precision, so as to avoid double exposure on any portion of the film.

FIG. 1.

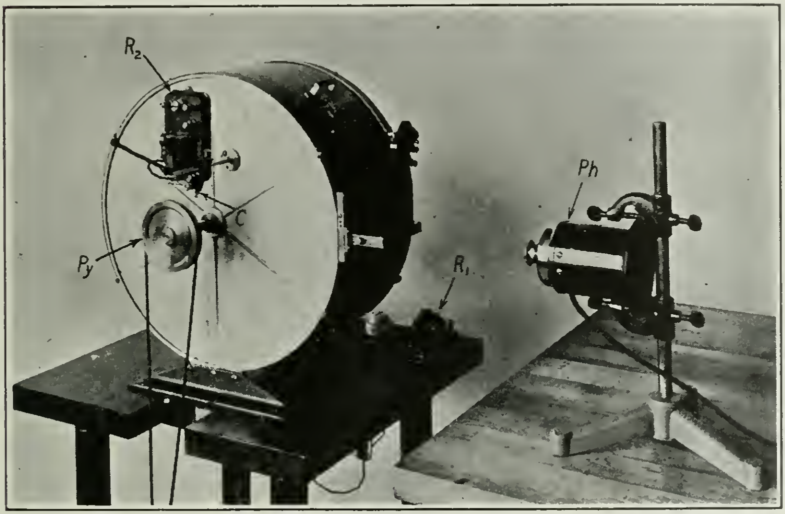


The high-speed oscillograph camera.

THE CAMERA.

The drum of our high-speed oscillograph camera is approximately five feet in circumference and four inches wide. It is mounted on a shaft, both ends of which protrude from a light-tight housing which in all dimensions, save its width, is just large enough to accommodate the drum without interference. The width of the housing is somewhat over eight inches, so that drum and shaft can be moved axially within it for a distance equal to the width of the drum. The film stretched over the periphery of the drum presents a cylindrical surface. By giving to the drum an axial as well as a rotational motion, the oscillograph record is traced on the film as a spiral band, similar to a screw thread. By moving the drum axially one-half inch per revolution and exposing the film through a width-limiting aperture one-half inch wide, placed before the shutter, a record forty feet long is obtained on a five-foot film.

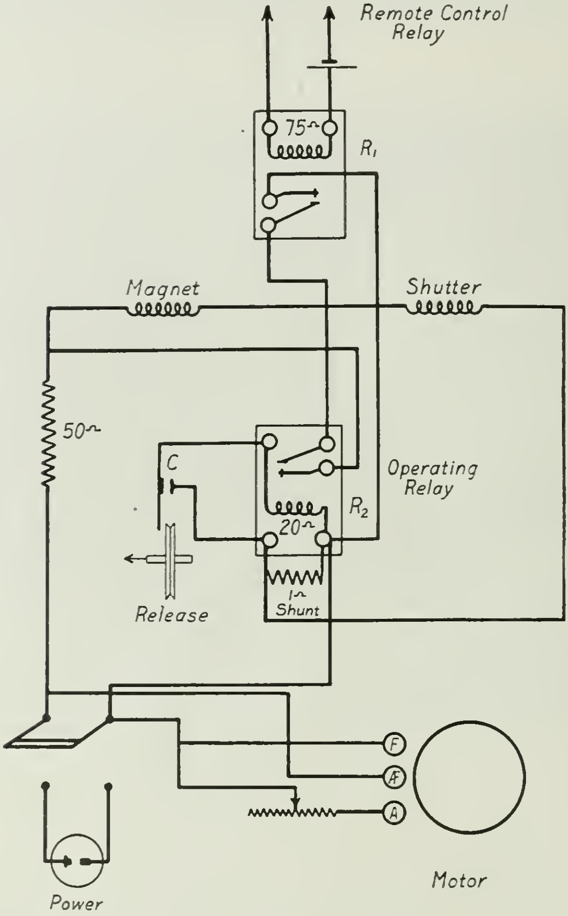
FIG. 2.



The camera set up to obtain oscillogram of loud-speaking telephone diaphragm motion.

The mechanism for securing this spiral motion is simple and positive in action. One end of the protruding shaft carries a phosphor-bronze worm *Wo* (see Fig. 1), the inner edge *E* of which rests against the bearing bushing *B* when the drum occupies its idling position in the housing. The driving pulley *Py* is on the other end of the shaft, as shown in Fig. 2. Except during exposure the cast-iron wheel *Wh* (see Fig. 1) idles on its shaft *Sh,* being driven by the worm *Wo.* The energizing of the magnet coil M causes the pole pieces P_1 and P_2 of the electromagnet to grip the cast-iron wheel, the idling motion of which is instantly arrested. The worm then necessarily feeds out along the wheel, thus imparting to the drum the desired axial motion. The cameras in our laboratory are equipped with readily interchangeable worm and wheel combinations, so that axial motions of either one-fourth or one-half inch per revolution may be had, corresponding respectively to sixteen and eight revolutions for a complete exposure.

FIG. 3.



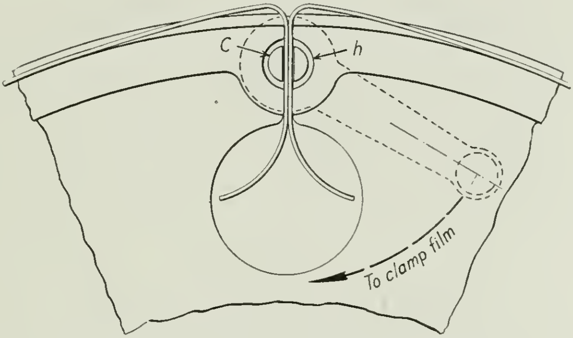
Wiring diagram of camera.

OPERATION OF THE CAMERA.

Ordinarily it is found convenient to use the camera in a dark room, as then the loading operation simply involves the turning off of the lights (with the exception perhaps of the safe light), the opening of the housing, the putting of the film in place, and the closing of the housing. The camera is then ready for use, and the lights may be turned on until the exposed film is to be removed for development.

If the work for which the camera is to be used is being prosecuted in a room the darkening of which is not feasible, preparation must be made for rolling the entire camera into the dark room, or else some sort of daylight-loading device must be provided.

Fig. 4.

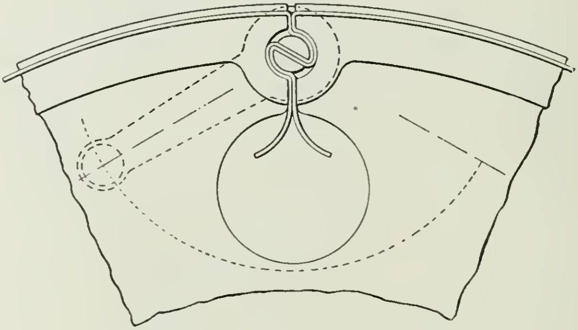


Film clamping device. Film ready to clamp.

With the loaded camera in position before the oscillograph the drum is brought to the desired speed. The exposure is begun by operating the relay R_2. Its operation energizes the wheel-gripping and shutter-opening electromagnets simultaneously, since their windings are connected in series. The exposure and the axial motion of the drum, therefore, begin simultaneously. After the drum has moved axially any predetermined distance, which may be all or only part of that available, the driving pulley *Py* whips open a contact *C*. The opening of this contact operates to restore the short-circuit across the two electromagnets. The closing of the shutter and the ceasing of the axial motion follow, again simultaneously. The power switch is then opened and the drum permitted to come to rest, whereupon the film may be removed for development.

The wiring diagram of Fig. 3 shows the electrical circuits of the camera designed for operation on a 220-volt power circuit. When the drum is idling preparatory to exposure the contact C and the contacts controlled by both relays are closed. The two relay contacts are in series and when closed short-circuit the coils of the two electromagnets. When the contact of relay R_1 is opened by operating the armature manually or by means of the remote control circuit the contact of relay R_2 also opens and is held open until the contact C is opened. The relay R_2 is provided with a shunt to avoid having contact C interrupt the whole current in the 220-volt circuit for the purpose of terminating the action. The same consideration has led to the short-circuiting of the electromagnets in lieu of opening the power circuit as a means of de-energizing them. As soon as C opens, the contact of relay R_2 closes (the contact of R_1 already being closed), and the short-circuit across the electromagnets is restored.

Fig. 5.



Film clamping device. Film clamped.

The manner of clamping the film on the drum is of some importance, partly because at high speeds the centrifugal action presents a problem and partly because the desired record may come where the ends of the film are joined. Both difficulties are overcome in a fairly satisfactory manner by the following device: A hole *h* about three-eighths inch in diameter is drilled through the thick rim of the drum parallel to the shaft direction (see Figs. 4, 5 and 6),[1] and a saw-cut about one-thirty-second inch wide is made through the rim, the cut passing through the axis of the hole. A split cylinder *C* terminating at one end in a small hand-lever fits the hole loosely. When a film is to be mounted, the slot in the cylinder is turned to coincide with that in the drum-rim and the end of the film is inserted into the channel formed by the lined-up slots. The drum is then rotated by hand, feeding the film into place. When the other end of the film is reached it is also inserted into the slot. The film is then adjusted to be reasonably taut by pulling with the hand the two film ends which protrude from the lower end of the slot. Fig. 4 shows the situation at this point. A turn is then given the hand-lever which puts the film under tension on the drum and simultaneously locks it in place. Fig. 5 shows the film position after this operation is completed. The relation of the clamping system to the drum is illustrated by Fig. 6.

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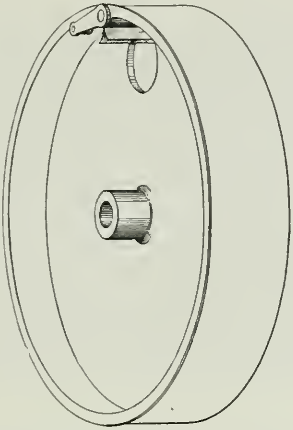
[1] I am indebted to Major W. P. Wilson of the Coast Artillery Corps for the preparation of these figures.

Fig. 6.



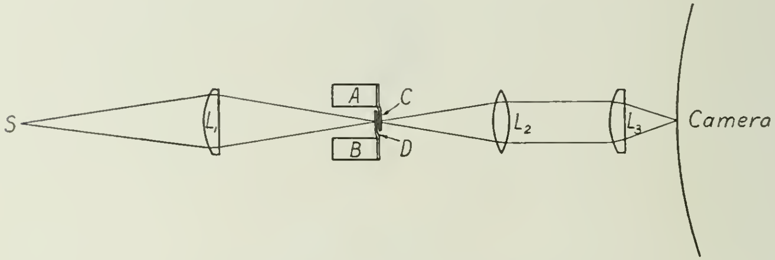
Relation of film clamping device to camera drum.

This method of clamping has been found quite adequate up to the highest film speeds which have been required, namely 100 feet per second. The ends of the film which serve for clamping are helpful in manipulating the film during development so that no portion of the film bearing the record needs to be handled. Finally, this method of clamping permits economy in the use of film. It serves equally well to clamp films of any width up to the full width of the drum. We have found a stock of film one inch, two inches, and four inches wide, convenient for general use in the laboratory. Frequently a one-inch film may be sufficiently wide to obtain all the record that is wanted and in general will be sufficient for making adjustments. The economy which this possibility of using narrow films involves is obvious. If films specially cut for use in the camera are not available it has been found convenient to use standard moving picture film cut into suitable lengths.

SMALL-TIME SCALE APPARATUS.

The two prongs, *a* and *b* (Fig. 7), of a tuning fork have mounted upon them light metal vanes, *c* and *d*, which overlap and move freely past one another when the tuning fork vibrates. These vanes are perforated by slits parallel to the prong length. The slits are two or three-thousandths of an inch wide and are adjusted to line up when the fork is at rest. If then light from a source S is focussed on the slit by means of lens L_1 the slits transmit light when the fork is at rest and an image of the slit may be thrown upon the film by means of the lenses L_2 and L_3. If the fork is caused to vibrate light will be transmitted only while the fork prongs are passing through their equilibrium positions and no light will reach the film from the source during the other phases of the motion. As the film moves, therefore, images of the slit will be recorded at distance intervals which are determined by the frequency of the fork and the speed of the film. Two images are produced for each cycle of the fork. A 500-cycle fork will, therefore, give rise to 1000 time lines per second. The distance between two such lines is the distance the film advances during .001 second. A typical record of such a time scale is shown in Fig. 8.

FIG. 7.

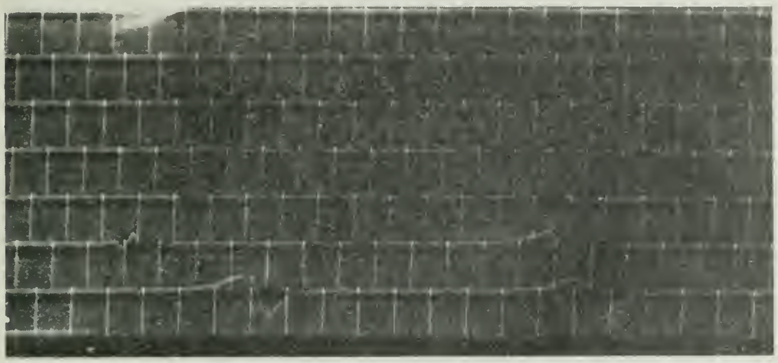


Tuning-fork time scale system.

In order that these time-scale lines shall be sharp it is necessary that the duration of coincidence of the slits shall be short compared to the duration of non-coincidence. This condition is in some degree brought about naturally by the fact that the prongs have their maximum velocities in passing through the equilibrium positions. It is improved by vibrating the fork at large amplitudes.

It may be worth pointing out that if the point of exact registry of the slits is not in the equilibrium position the recorded time intervals for successive half-periods will not be the same. This condition is remedied by adjusting the slits or sometimes more easily by using only the alternate timing lines on the film in making the measurements.

FIG. 8.



Typical time-scale record.

The advantages of a time scale of this character over a sinusoidal trace are rather obvious. To obtain any precision with the latter, it is necessary to draw chords parallel to the time axis and to bisect the chords in order to determine the exact position of the crests of the sinusoidal wave. The time lines may be looked upon as the equivalents of these bisectors experimentally obtained.

This method of obtaining a time scale did not originate in our laboratory. It was used by Prof. D. C. Miller,[2] in his phonodeik records and extensively by Doctors Curtis and Duncan[3] in connection with the G.E. oscillograph. Fig. 9 shows a 500-cycle fork equipment mounted on the G.E. oscillograph of the Sound Laboratory. The optical arrangements can be easily followed by means of the light beam sketched into the figure. The electrical arrangements for driving the fork will be discussed later.

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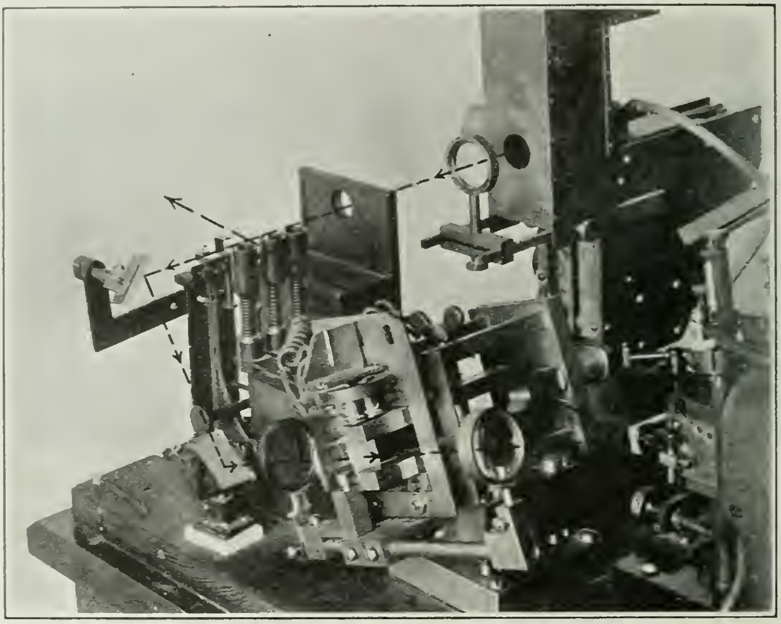
[2] D. C. MILLER, "The Science of Musical Sounds," Macmillan, 1916.

[3] H. L. CURTIS and R. C. DUNCAN, *Jour. Wash. Acad. of Sc.*, Vol. 9, p. 642, 1919; *Phys. Rev.*, 2nd Ser., Vol. 15, pp. 511, 512, 1920.

The incorporation of the timing system into the oscillograph as an integral part has the disadvantage of necessitating the equipment of each type of oscillograph. The difficulty is avoided by making the timing system a part of the camera. A unit of this kind is shown in Fig. 10. The upper plate of the part which functions both as lens housing and light shield has been removed and a light ray traced in to indicate the functioning of the optical system. For high film-speeds the concentrated-filament lamp shown in the figure must be replaced by an arc lamp.

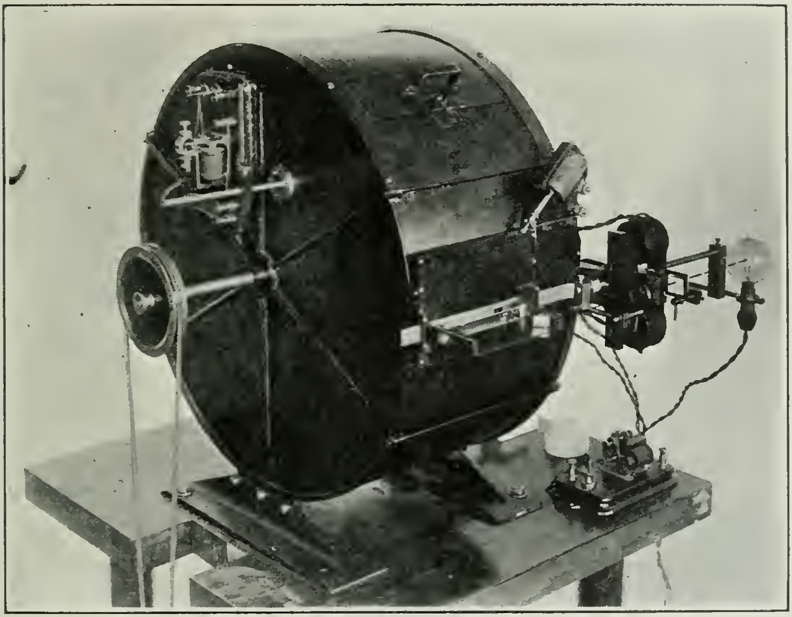
FIG. 9.



Tuning-fork equipment of G.E. oscillograph.

Precise measurements require a close time scale, that is, many time index marks. In this way only can the errors due to unequal shrinkage of the film and non-uniform film speeds be reduced to a minimum. In our work we have found one time line per centimetre adequate for most purposes. At a film speed of one metre per second a 50-cycle tuning fork will give this spacing. At a film speed of ten metres per second a 500-cycle fork will be required.

Fig. 10.

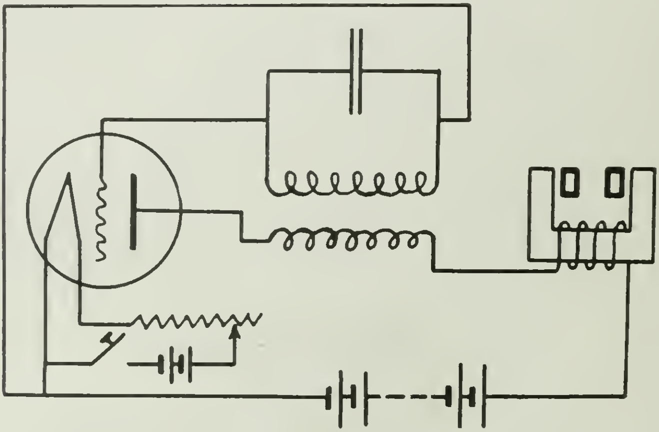


Camera with timing system incorporated.

It is well known that the difficulties of maintaining the vibrations of a tuning fork increase very rapidly with the frequency of the fork. Lord Rayleigh met the situation by driving a high-frequency fork by means of a low-frequency master fork. In this method the driving coils of the two forks are connected in series and the interruptions of the current are controlled by means of a contact on the master fork. The frequency ratio of the forks must be adjusted to be an integral number. Doctors Curtis and Duncan in this manner maintain the vibrations of a 500-cycle fork by means of a 100-cycle master fork.

The master-fork method of maintaining the vibrations of a high-frequency fork has several practical disadvantages. The adjustment of the frequency ratio to an integral number is not permanent owing to a variety of causes, and the making of the adjustments is sometimes tedious, particularly when the frequency ratio is high. Furthermore the experimental difficulties increase very rapidly with the frequency for frequencies much above 500 cycles.

FIG. 11.



Idealized electron tube circuit for tuning-fork drive.

It occurred to us several years ago that the methods then available for obtaining sustained electrical oscillations by means of an electron tube might be available for maintaining the vibrations of a tuning fork. Our preliminary experiments had already been somewhat successful when we found that two British investigators, Eccles and Jordan,[4] had reached the objective and had published an account of their experiments. We have gradually developed this method of sustaining tuning-fork vibrations and are finding it remarkably reliable and convenient in connection with our time measurements.

The idealized circuit arrangement for this type of tuning-fork drive is shown in Fig. 11 and the actual driving arrangement diagrammatically in Fig. 12. The d.c. component of the plate current magnetizes the laminated yoke with reference to which the fork prongs are so arranged that their motion will cause a maximum change of the reluctance of the magnetic circuit. An adjustment is provided for varying the position, with respect to the yoke, of the laminated core which carries the grid coil. This control of the electromagnetic coupling between the grid and plate circuits constitutes an important practical advantage. The essentials of this type of tuning-fork drive have been described by Eckhardt, Karcher and Keiser.[5] A working unit is shown attached to the high-speed camera in Fig. 10.

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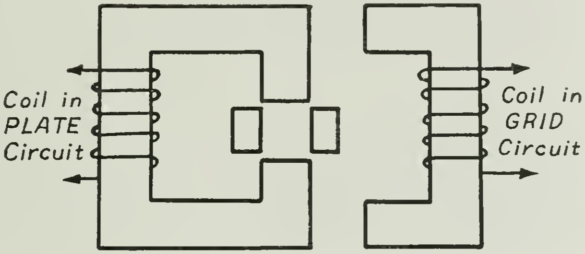
[4] W. H. ECCLES and F. W. JORDAN, *The Electrician*, Vol. 82, p. 704, 1919.

With reasonably constant voltages the electron-tube drive is very satisfactory and the constancy of the frequency obtained has been checked in a large number of experiments.

FIG. 12.



Actual tuning-fork driving arrangement.

USES OF HIGH-SPEED OSCILLOGRAPH.

In Fig. 2 the camera is shown set up to obtain an oscillogram of the diaphragm motion of the loud-speaking telephone *Ph*. The linear motion of the centre of the diaphragm was converted into angular motion of a tiny mirror by the method used by Professor Webster in his phonometer. In this case the time-scale apparatus was not used, the wave form of the diaphragm motion being the point of interest. A record of the motion at a frequency of 4096 cycles is shown in Fig. 13. Records of the vibrations of a relatively massive system obtained in connection with a fatigue test of metals are shown in Fig. 14. In this case the system itself had sufficient angular motion to obtain the records shown. In Fig. 15 the camera is shown before the G.E. oscillograph of the Sound Laboratory and in Fig. 16 it is shown set up to coöperate with an Einthoven galvanometer. These figures indicate briefly the range of availability of the high-speed oscillograph camera.

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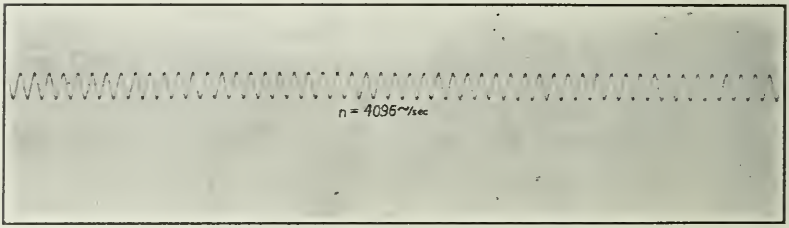
[5] E. A. ECKHARDT, J. C. KARCHER and M. KEISER, *Phys. Rev.*, 2nd Ser., Vol 17, pp. 535, 536, 1921.

The precision of time measurement attainable is determined by the accuracy of the value used for the fork frequency and the character of the record obtained. The fork frequency is determined by recording the breaks of a break-seconds chronometer against the tuning-fork time scale. The frequency is then determined by counting the number of timing line intervals included between two chronometer breaks. When this is done the interesting fact comes to light that although the chronometer keeps excellent time on the average the individual seconds vary by several parts in a thousand. The same seconds interval, for example, that from the fifteenth to the sixteenth, as indicated by the seconds hand, will repeat much more closely. To get an accurate value it is therefore necessary to measure every second in the minute and to repeat these measurements to check each second. In this manner the frequency of the fork may be obtained to one part in ten thousand.

Fig. 13.



Oscillogram of diaphragm motion of loud-speaking telephone.

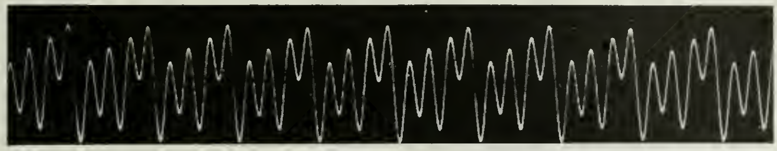
The use of several different chronometers in such calibrations has indicated marked differences in the uniformity of the seconds intervals in different instruments and the method commends itself for the testing of the quality of break-circuit chronometer instruments.

In closing, it may be of some interest to outline briefly one or two problems, the solution of which was facilitated by the use of the apparatus described.

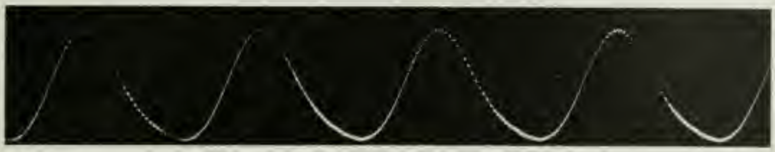
COOLING TURBINE ON MACHINE GUN.

A proposal was made by someone that the air cooling of a machine gun could be improved by having a turbine propelled by the powder gases draw air past the barrel at an increased rate. The type of motive power was somewhat unusual and designers wanted clues as to the efficient design of such a system. Several model turbines were built and tried and the question came up,

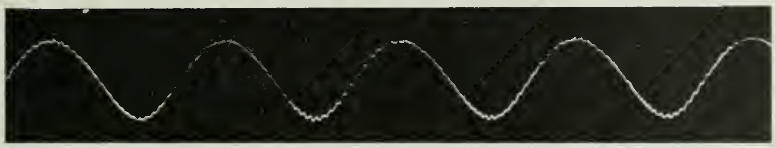
Fig. 14.



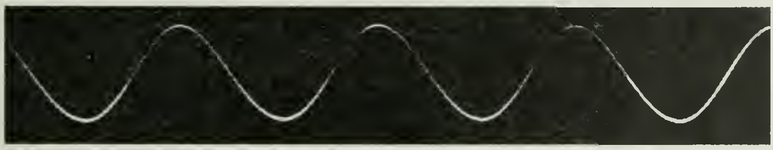
Strong low harmonics.



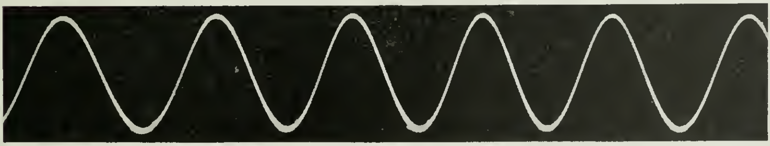
Low and weak high harmonics.



Strong high harmonics.



Weak high harmonics.

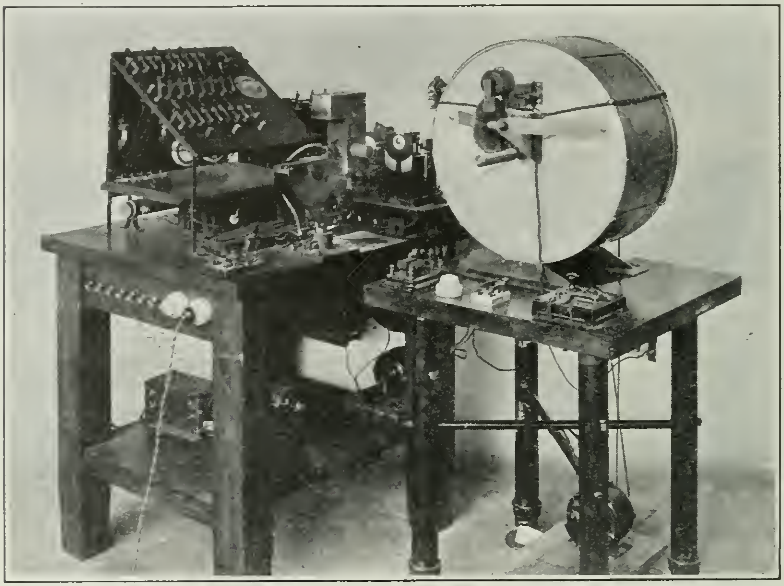


Satisfactory adjustment. Practically pure sine wave.

Oscillograms of flexural motion of massive mechanical vibrating system.

"What maximum speed do these turbines attain and in what time is it obtained?" After considering the problem we concluded that it would be feasible to have the turbine close a properly designed contact once every revolution and thus a record of the duration of each revolution could be obtained. After some preliminary difficulties with the contact, satisfactory records were obtained from which the relation between the r.p.m. of the turbine

FIG. 15.



Camera with G.E. oscillograph.

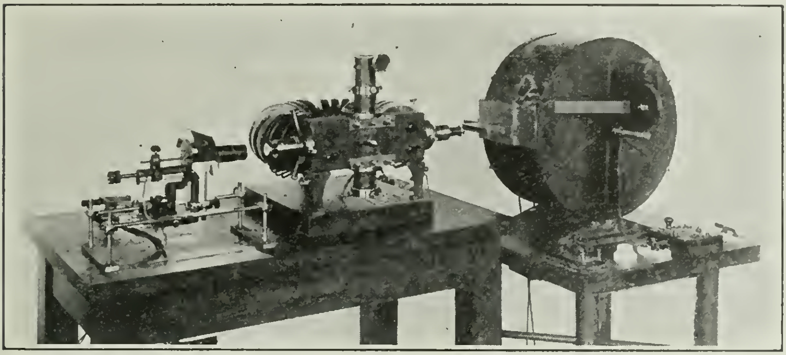
and the time were deduced. The results of one such record are shown in Fig. 17. It indicates that the turbine reached a speed of nearly 24,000 r.p.m. in less than four seconds. At this point the fire ceased and we have the logarithmic decay curve of the rotating system coming to rest. Only a few of the many points obtainable from the records are indicated on the curve, these being sufficient to indicate the character of the acceleration.

The rate of fire was slightly below ten shots per second, so that the curve relates to the firing of a burst of thirty-seven shots. The impulse due to each shot is readily discernible in the record by the markedly shorter time of the next succeeding revolution.

THE NAVAL OBSERVATORY—ANNAPOLIS TIME LAG.

As a matter of regular routine the Annapolis radio station sends out time signals twice daily, from 11:55 A.M. to noon, and from 9:55 to 10:00 P.M. In the telephone of a radio receiving set one hears a sound of one frequency for approximately two-thirds of a second and another frequency for one-third of a second, alternating regularly very much like the "cuckoo" of a cuckoo clock. At the half minute one alternation is omitted and just before the minute five alternations. At the end of the five minutes ten alternations are omitted, that is, the pitch remains constant for ten seconds and then follows a long dash signal at the other pitch broadcasting 75th meridian noon and 10:00 P.M. at their respective times.

FIG. 16.

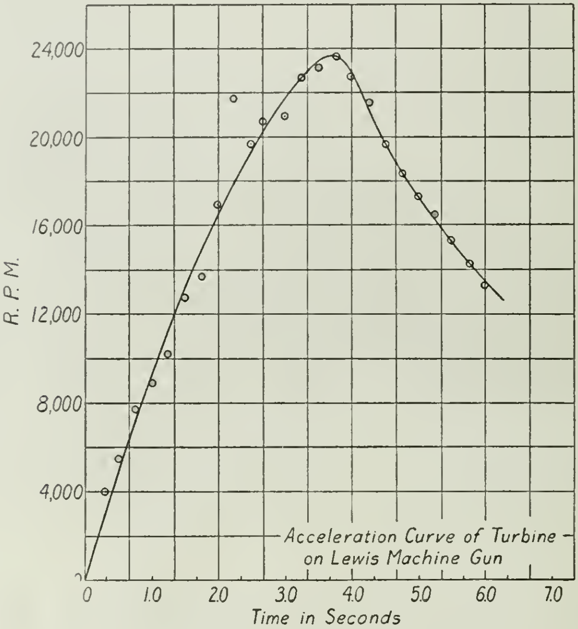


Camera with Einthoven galvanometer.

These signals are controlled automatically from the Naval Observatory at Washington, District of Columbia. Between the controlling clock and the radio transmitting set there are a number of relays which necessarily cause a lag of the radio signal behind the impulses of the controlling clock. In the affairs of everyday commerce a lag of a few hundredths of a second is of no importance, but there are cases in which such magnitudes need to be considered. One such case is the precise determination of longitude.

If the Annapolis noon signal is received at a place at precisely 1:00 P.M. local mean solar time we know that this place is 15° of longitude east of the 75th meridian. Two points, four geographical miles apart along the equator of the earth, have a difference in mean solar time of one second. An error of .01 second in time would make a change of something over 243 feet in the longitude determination. In view of the development of automatic radio transmission and reception the times can be obtained so accurately that longitude determinations to within a few feet are being considered. There remains as a possible source of error the lag in transmission. This error can be largely eliminated if the lag is actually measured and the degree of its constancy established.

FIG. 17.



Time-speed curve of high-speed turbine.

In April, 1920, the U. S. Navy was coöperating with the British Admiralty in a longitude determination of this kind in Australia in which the 75th meridian and 75th meridian time were to serve as reference marks. Special time signals were sent out daily for a week from 2:00 to 2:15 P.M. The question of determining the lag was submitted to us and we made the attempt on less than a day's notice. The only oscillograph instrument available for the purpose was a string galvanometer which had been giving considerable trouble because of its inadequate damping, and this defect proved a considerable handicap since in the first records we found that the two phenomena, the interval between which we wished to establish, overlapped hopelessly on the record.

We overcame this difficulty by using an auxiliary clock during the transmission. The seconds beats of this clock were displaced with respect to those of the transmitting clock sufficiently to avoid this interference.

The following records were obtained:

1. Transmitting clock *vs.* auxiliary clock, five minutes prior to time signals.
2. Radio time signals *vs.* auxiliary clock.
3. Transmitting clock *vs.* auxiliary clock, five minutes after time signals.

To go into the results would exceed the limits of this paper. The values obtained, however, show that there are real variations in the lag which are of the order of .01 second, the lag itself being roughly .06 second. The observed variability indicates that in connection with precise longitude work the lags should be measured for each signal used in the determination.

Our work in this connection consisted simply in the experimental determination of the lag. We supplied the results to the U. S. Naval Observatory which was handling all other matters in connection with the longitude determinations.

In conclusion it is a pleasure to acknowledge the valuable contributions of my associates, Dr. J. C. Karcher and Mr. M. Keiser, who, no less than the writer, are responsible for the development of the apparatus and for its successful use in the solution of many interesting problems.

Eye Injuries in Industries.—The number of accidents resulting in the loss of one or both eyes by workers is very great, and strong efforts have been made to reduce them by the use of goggles. A good deal of experimenting has been done to secure satisfactory glass and some excellent forms have been produced. Workers are, however, not always favorable to their use, and run risks which often result in injury. In a recent bulletin of the National Committee for the Prevention of Blindness, issued from its office in the Russell Sage Foundation Building, it is stated that good work has been done in this line, and that the importance of the use of goggles has been impressed more widely upon workers. This is good news, for recent publications of the organizations interested in accident prevention have been to the effect that there has been a marked slackening of attention to the subject on the part of many industrial establishments. Safety provisions and insistance on the use of safety appliances have been discontinued in many places, and the working conditions allowed to drift into the old careless methods of former years. This is to be regretted, but the cause is doubtless largely with the worker, who is very apt to become indifferent to the dangers of the occupation. "Familiarity breeds contempt" and also breeds indifference. It is stated in the bulletin above noted that in five years 3000 persons each lost an eye in the industries of Pennsylvania. The proper and persistent use of goggles would probably have diminished this figure very much. Full details concerning eye hazards in industries and the means of reducing or eliminating them will be presented in a revised edition of Bulletin 12, shortly to be issued by the National Committee. Several forms of posters, calling attention to dangers to the eyes and the methods of protection, have been distributed by the Committee.

H. L.

Egyptian Ink.—A. LUCAS (*Analyst*, 1922, xlvii, 9–15) has analyzed a sample of dried black ink which was contained in an inkstand of the time of Amenhotep III (sixteenth century, B.C.), and was approximately 3500 years old. The pigment in the ink was carbon; iron was absent. Carbon for ink has been made in Egypt by the destructive distillation of date stones, and by the incomplete combustion of incense. Inks, made from low-grade carbon and containing tar-like impurities, may yield a brown or partly brown color when used for writing. Iron inks apparently were first used during the seventh or eighth century, A.D. J. S. H.

Natural Sodium Compounds and Borates in 1921. (*Press Notice U. S. Geological Survey*, June, 1922.)—The production of natural sodium compounds in the United States in 1921 amounted to 25,000 short tons, valued at $894,000, according to reports of the producers to the United States Geological Survey. This was a decrease of about 41 per cent. in both quantity and value. The material marketed was sodium carbonate (soda ash) from Cartago and Keeler, Inyo County, California; sodium bicarbonate from Keeler, Inyo County, California; sodium sulphate (Glauber's salt) from Lake Point, Salt Lake County, Utah, and Casper, Natrona County, Wyoming; sodium borate (borax) from Trona, San Bernardino County, California; and trona (a double salt of sodium carbonate and sodium bicarbonate) from Trona, San Bernardino County, California.

The production of boron ores in 1921 was approximately 50,000 short tons, valued at $1,320,000. This represents a decrease of over 58 per cent. from the quantity shipped in 1920. The output was borax (sodium borate) from Trona, San Bernardino County, California, and colemanite (calcium borate) from Death Valley Junction, Inyo County, and Lang, Los Angeles County, California, and Dike, Clark County, Nevada. R.

ADDITIONAL NOTE ON SO-CALLED APLANATIC OPTICAL SURFACES AND LENSES.*

BY

JAMES P. C. SOUTHALL.

Professor of Physics, Columbia University, New York.
Member of the Institute.

SINCE the publication of my recent paper on "Aplanatic (or Cartesian) Optical Surfaces"[1] I have obtained, mainly from two sources, certain new information in regard to both the history of these surfaces and their modern applications, which would certainly have been included in the previous paper if I had been in possession of it at that time, and which seems to me to be of sufficient importance to warrant an additional note on the subject. The sources to which I allude are two well-known German works, one on the history of Optics published in 1838, and the other on modern optical instruments published nearly three-quarters of a century later in 1911; both of which I have often before had occasion to consult. Indeed, paradoxical as it seems, my very familiarity with each of these books is perhaps responsible for the fact that it had not occurred to me previously to suppose that either of them would throw any new light on the Cartesian surfaces and lenses.

The first work is Dr. Emil Wilde's "Geschichte der Optik" (Berlin, 1838) which contains a long chapter on Descartes, whose chief contributions to optical science are to be found in his famous treatise on "Dioptrique."[2] Now that the true law of refraction had been at last discovered, Descartes naturally regarded it as a matter of much importance to determine, theoretically at least, the most advantageous forms of the surfaces of optical glasses; and having proved that a cylindrical bundle of incident rays which were parallel to the axis could be converged accurately to a real focus either by a convex meniscus sphero-elliptic glass lens or by a planoconvex hyperbolic glass lens, he unhesitatingly recommended one of these forms as being decidedly superior to the ordinary type of lens with both faces spherical, because under the same circumstances the ordinary type would necessarily have the fault of showing spherical aberration along the axis. In the same way also it was possible to design negative or divergent glasses which under the same conditions as before would likewise be free from spherical aberration, namely, a concave meniscus lens with an ellipsoidal surface concave towards the beam of parallel rays, the other surface being spherical, and a planoconcave hyperbolic lens placed so the parallel rays will fall perpendicularly on the plane face. Of the two types of lenses Descartes preferred the hyperbolic form as being both simpler and cheaper to manufacture. So confident was he of the enormous advantage to be gained by this method of construction that he believed it might even be possible to make a telescope which was so perfect optically that it would reveal the very details on the stars! Accordingly, he spent much mathematical ingenuity in trying to suggest mechanical contrivances for aiding opticians in grinding the requisite aspherical surfaces. When he was in Paris in 1628 he found there a man named Ferrier who actually succeeded in making for him a convex hyperboloidal glass surface; but as all his efforts to obtain a similar concave surface were in vain, Descartes was obliged to abandon the project of combining these lenses in a Dutch telescope (which is the only type of telescope which he discusses in the ninth chapter of the treatise above mentioned). Sir Constantijn Huygens, the father of Christiaan Huygens, was a friend of Descartes, and he endeavored to have these Cartesian lenses ground by some skilled Dutch opticians, equally without success. It is a little singular how much importance Descartes himself attached to this matter, especially as he knew that even if his hyperbolic lens were free from spherical aberration along the axis, it might not be as good as an ordinary lens for reproducing object-points which were a little off the axis. Moreover, the big difficulty in those early days when the telescope was still in its infancy was not so much the fault of spherical aberration as the far more serious matter of chromatic errors which not all the genius of Newton could overcome, so that he finally invented an entirely new kind of telescope to get around this fundamental trouble. The fact is that these Cartesian lenses may give exceedingly poor optical images even in monochromatic light. Nevertheless, by suitable combinations of a pair of them it is possible to re-unite at any prescribed point all the effective rays belonging to a given point of an object, no matter whether the two points are real or virtual, one or both.

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* Communicated by the Author.

[1] JOUR. FRANK. INST., 193 (1922), pp. 609–626.

[2] René Descartes: "Discours de la méthode pour bien conduire sa raison, et chercher la verité dans les sciences; plus La dioptrique, Les meteores et La géométrie," Leyde, 1637.

In my previous paper I remarked that Kepler, without knowing the true law of refraction, had somehow discovered the aplanatic property of an hyperbolic spheroidal refracting surface for rays proceeding in the denser medium parallel to the transverse axis of the hyperbola. In the same connection it deserves to be noted also that in proposition LX in his "Dioptrice" (Augsburg, 1611), Kepler explains with extraordinary perspicacity the mechanism of vision in the human eye and rightly conjectures that the image is focused on the sensitive surface of the retina, although J. B. Porta (1543–1615), who had compared the eye with a *camera obscura,* supposed that the image was formed in the crystalline lens itself. But Kepler even imagines that the crystalline humor is a convex lens with an hyperbolic posterior surface for the purpose of producing a more perfect convergence of the rays and consequently a sharper image on the retina.

The other book to which I alluded above is Dr. Alexander Gleichen's "Theorie der modernen optischen Instrumente" (Stuttgart, 1911) which has recently been translated in English.[3] The last chapter of this useful and original volume is on "Aplanatism," where, however, the author is careful to distinguish between a "Cartesian system" and an "aplanatic system" in the usual modern meaning of the latter term. Following Abbe, Gleichen used the word "aplanatic" to describe "a centered optical system which produces aplanatic imagery for all zones over a finite aperture," and which, therefore, besides being free from spherical aberration with respect to the axial point of the object, likewise satisfies Abbe's sine-condition. Gleichen refers to Descartes' "Dioptrique" and indicates how the equation of the Cartesian optical surface of the fourth degree in x and y is obtained; and likewise he calls attention to the fact that in certain special cases, particularly when one of the foci is infinitely far away, this equation reduces to one of the second degree and represents therefore a spheroid generated by the revolution of a conic section around the optical axis. "Beyond doubt," says Gleichen, speaking of these surfaces and other forms of aspherical optical surfaces, "aplanatic systems are destined to play an important part one day in technical optics as soon as methods have been devised for grinding the lenses with the same degree of accuracy with which spherical surfaces can be ground at present."

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[3] "The Theory of Modern Optical Instruments," by Dr. Alexander Gleichen, translated from the German by Messrs. Emsley and Swaine, and published for the Department of Scientific and Industrial Research by His Majesty's Stationery Office, London, 1918. (A new impression of this book has been issued perhaps within the past year.)

The aplanatic meniscus lenses with both faces spherical, which are described by Gleichen in detail, utilize the property of the well-known pair of aplanatic points of a spherical refracting surface. This remarkable pair of points was discovered first by Huygens and is mentioned by him in a letter to his former teacher Franc. van Schooten, in which he communicated the fact that under certain circumstances "one of the ovals which Descartes had conceived for re-uniting the rays reduces to the circumference of a circle."[4] Huygens himself has described fully the aplanatic meniscus lenses "of the first type," as Gleichen calls them.[5]

But by far the most interesting part of Gleichen's chapter on "Aplanatism" is the section entitled "Semi-aplanatic lenses made by Zeiss," in each of which one of the surfaces is plane or spherical while the other surface is aspherical. They are called "semi-aplanatic" because they are not completely aplanatic in the restricted meaning of the term; either the spherical aberration having been abolished for all zones and the sine-condition being satisfied for one zone, or *vice versa*. Gleichen gives a table with the numerical constants for twenty-four semi-aplanats of this kind, each of focal length $f = 100$, and also diagrams of six of them. A point to be noted in practically all these various types is the relatively small aperture and great thickness of the lens, which apparently limits its usefulness.

In conclusion Gleichen remarks again that "the employment of aplanatic, semi-aplanatic or Cartesian systems might be adopted more widely than heretofore with the development of the technique of glass working," and that it may be quite possible that "along these lines a revolution in technical optics lies before us." Several modern applications of so-called aplanatic optical combinations are instanced by Gleichen, namely, in "searchlight systems," "complex condensers for projection purposes," and "aplanatic field lenses;" not to mention the employment of "deformed" surfaces for special corrections, as, for example, in the so-called "Katral" spectacle lens and in the illumination system and receiving system of Gullstrand's ophthalmoscope.

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[4] "Œuvres complètes de Christiaan Huygens publiées par la Société Hollandaise des Sciences." Tome treizième, "Dioptrique" (La Haye, 1916), p. 48. See also Huygens's "Treatise on Light," translated by S. P. Thompson (London, 1912), p. 114.

[5] *Loc. cit.*, pp. 64–66.

DEPARTMENT OF PHYSICS,
COLUMBIA UNIVERSITY, NEW YORK,
May 8, 1922.

The Activation of Hydrogen.—Over a year ago Wendt and Landauer, of the University of Chicago, found that an unstable and active modification of hydrogen can be obtained by three methods: The action of alpha rays; alternating discharge at low pressures, and passage through the corona at ordinary pressure. Rays in the Schumann region produce no effect. The activity is not due to ions nor to atoms. A contraction in volume takes place which suggests an analogy to that which occurs in the activation of oxygen, and leads, therefore, to the view that the activated hydrogen is triatomic. The investigators have presented certain theories upon the subject. Independently of Wendt and Landauer a similar change in hydrogen was observed by Y. Venkataramaiah of the Indian Institute of Science at Bangalore. The experiments were made with detonating gas containing an excess of hydrogen. The mixture was submitted to the silent electrical discharge in an ozonizer and the mixture after leaving the ozonizer was passed through an alkaline solution of potassium permanganate. In the course of the experiment an electric spark accidentally occurred, which caused an explosion, destroying part of the apparatus, but the whole of the permanganate solution immediately turned green. It was at once suspected that this action might be due to a marked increase in the reducing power of the hydrogen, inasmuch as ordinary hydrogen brings about such a change very slowly. A Hofmann eudiometer was filled with an alkaline solution of the permanganate and a few cubic centimetres of the detonating gas with excess of hydrogen were introduced. Electric sparks were produced in the mixture and the solution turned green. Further studies showed that an alkaline solution of indigo is bleached, ferric chloride is turned into ferrous, potassium nitrate into nitrite, arsenous acid into hydrogen arsenide, potassium perchlorate into potassium chloride. Other similar reactions were observed.

References to the literature show that in 1913 Sir J. J. Thomson made observations indicating the production of particles having an atomic weight of three, presumably hydrogen. Duane and Wendt found in 1917 that the influence of alpha particles from radium emanation produces a contraction of volume in hydrogen. In 1912, Langmuir produced an active modification of hydrogen by heating a filament in the gas at low pressure. Further observations on this modification have been presented by the Indian investigators, and the American observers are also working along this line. The results of the investigation in India are published in the bulletin of the Science Association of the Maharajah's College, Vizianagram.

H. L.

Standard Colors for Traffic Signals.—A conference on the standardization of colors for traffic signals was recently held in New York under the auspices of the American Engineering Standards Committee. Representatives were present from practically all of the national engineering societies, safety associations, electric and steam railway interests, automobile dealers, manufacturers and users associations, police and traffic departments, insurance companies, and several departments of the federal government.

It was agreed unanimously "that there should be national uniformity in the use of colors for signals," and that the detailed technical work involved in bringing this about should be by a sectional committee under the auspices of the American Engineering Standards Committee. Included in the scope of the work were the following:

The use of colored lights on all highway vehicles.

Their use on all signals along highways and at curbs, both permanent and temporary.

Their use for highway crossing signals for steam and electric railways.

A coördinated relation of color, form, position and number of signals.

A coördinated relation to system of flashing, moving or other similar lights.

Colors for non-luminous as distinguished from luminous signals.

Recommendations on the use of colors for emergency exit signals.

Methods of specifying or defining colors for signal purposes.

Any other closely related matters which, in the opinion of the sectional committee, form a part of the subject to be considered.

A suggestion that yellow light be used in place of red for the tail light of automobiles brought forth a spirited discussion.

The conference did not advocate the substitution of green for red as a danger signal, as was erroneously reported in some daily papers due to misinterpretation of discussions. On the contrary, the ideas expressed at the conference were emphatic that red should be used to indicate danger and for no other purpose. In conformity therewith, it was suggested that green be substituted for red as the color for lights for emergency exits of public buildings as indicating paths that lead to safety.

H. L.

CONTRIBUTIONS TO THE CHEMISTRY AND TECHNOLOGY OF GELATIN AND GLUE.*†

BY

ROBERT HERMAN BOGUE, Ph.D.

Industrial Fellow of the Mellon Institute of Industrial Research of the University of Pittsburgh, and Research Chemist for Armour and Company of Chicago.

In the first of these, the gelatin solutions were subjected to viscosity measurements at varying temperatures and under varying speeds of rotation (using the MacMichael viscosimeter) to determine if evidence of plastic flow could be observed. It was found that in a 25 per cent. solution, plastic flow first became manifest at about 34° C. This was indicated by the fact that an extrapolation of the viscosity-r.p.m. curves met the axes at the origin at temperatures above 34°, but below this temperature the intercept occurred at increasing distances from the origin on the viscosity axis. This is illustrated in Fig. 13. At lower concentrations the transitional temperature appears also to be lower.

The other series of experiments consisted of a measurement of the change in viscosity with time of gelatin solutions at varying H-ion concentrations and under different degrees of purity. The data, illustrated in Fig. 14, show that at 35° C. the viscosity of a normal gelatin decreases with time except at *pH* 4.7. The viscosity of the ash-free sample increased slightly with time at 35°, but was constant at 37°.

The first of these experiments indicates that the transition from the sol to the gel condition is a gradual and not a sudden change, such as occurs for example when a crystal of benzol changes to the liquid phase, and that the measurability of the change is a concentration variable. The second experiment indicates that there are several factors influencing the effective volume of the gelatin in the solution. These include the H-ion concentration, the amount and nature of the inorganic ions present, and the products of gelatin hydrolysis.

In 1920, the writer[63] outlined his views upon the structure of gelatin-water systems. There has since that time been so much work of a more or less confirming character that it seemed desirable to restate the theory, and to add thereto further postulations based upon recent work.[64]

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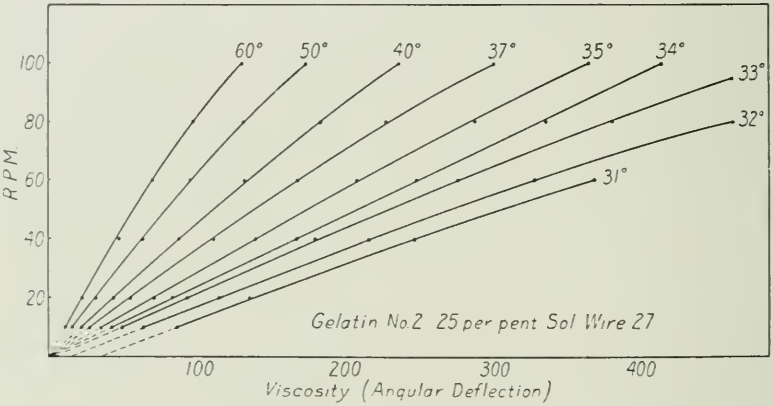
* Communicated by Dr. E. R. Weidlein, Director, Mellon Institute of Industrial Research of the University of Pittsburgh.

† Concluded from Jour. Franklin Inst., June, 1922, p. 825.

[63] R. H. Bogue: *Chem. Met. Eng.*, 23 (1920), 61.

Gelatin sols appear to consist of slightly hydrated molecules united together into short threads[65] resembling streptococci. These threads are probably very short, but should be capable of exhibiting mechanical elasticity roughly proportional to their length. Procter[66] thinks that at 70° C. the solution becomes probably nearly molecular.

FIG. 13.



Viscosity-plasticity curves.

A lengthening of these threads seems to take place as the temperature falls, and at the same time the water-absorbing power of the gelatin increase.[67] This accounts for the rapid increase in the viscosity with drop in temperature. At temperatures above 40° C. the change in length of thread or water absorption, per unit change in temperature, is small, but at 30°–20° the change is very great. A solid jelly will result only when the relative volume occupied by the swollen molecular threads has become so great that freedom of motion is lost, and the adjacent heavily swollen aggregates cohere. The rigidity seems to depend on the relative amount of free solvent in the interstices of these aggregates, and on the amount of solvent that has been taken up by the gelatin in a hydrated or imbibed condition. The resiliency or elasticity is probably dependent upon the length and number of the catenary threads. A solution, or change from the gel to the sol form, may result only through the reversal of these processes. That is, a release of a part of the water retained by the heavily swollen molecules, and a partial disintegration of the long enmeshed fibrils of the gel. Any tendency on the part of the fibrils towards an orientation would imply an attractive force between

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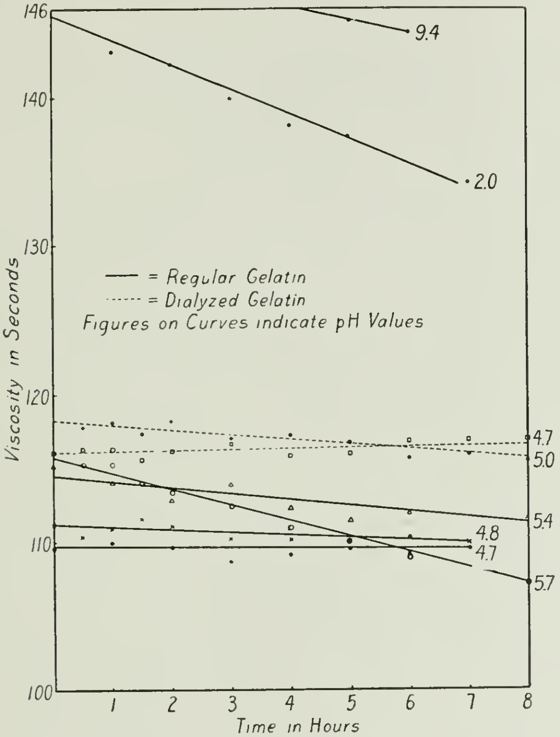
[64] R. H. Bogue: *Loc. cit.*

[65] J. Loeb has found the assumption of a few united molecules to account for the differences in the osmotic pressures of calcium and sodium gelatinates. (*J. Gen. Physiol.*, 1 (1919), 496.)

[66] H. R. Procter: *Cf.* Ref. 40, p. 41.

[67] Whether or not this is real hydration is undetermined. McBain and Salmon (*J. Chem. Soc.*, **119** (1921), 1374) have reported an increase in hydration of soap upon a lowering of the temperature. H. C. Jones (*Z. physik. Chem.*, **74** (1910), 325) has shown that the hydration of molecules and ions increases with a fall in temperature.

FIG. 14.



Change in viscosity with time at varying pH 2 per cent. solution, 35°C.

them which would result in a shrinkage. This becomes manifest in syneresis. That some such orienting force does exist is indicated by the lenticular form of bubbles that are generated within gels. The degree of swelling that may be produced in cold water or electrolyte solutions is determined by osmotic forces, as described by Procter, and may be controlled by observing the principle of the Donnan Equilibrium as shown by Procter and by Loeb.

It appears that the colloid fibril consists at elevated temperatures of but a few partially hydrated molecules attached to each other, and floating about as discrete particles in the solvent. An increase in viscosity with time would then signify either an increase in the size (length) or number of the threads, or an increased volume due to the absorption of water or hydration. At elevated temperatures, the equilibrium is evidently rapidly attained. This seems to be due to the relatively small changes that are induced in the particle size and degree of water absorption or hydration by variations in temperature at *elevated temperatures,* and to the high mobility of the free solvent. But as the temperature falls, the amount of change per unit drop in temperature increases rapidly, and with this a rapid decrease in the mobility of the solution through the withdrawal of the solvent by absorption or hydration. The time required for the colloidal molecule-fibrils to reach a state of complete equilibrium with the solvent is consequently vastly increased. In other words, the solution will show an increase in viscosity with time.

Under any given condition of temperature and hydrogen ion concentration there will be a certain condition of viscosity which the system will attain at equilibrium. A temperature at which no change in viscosity with time occurs indicates an immediate equilibrium condition, but this temperature will vary with different hydrogen ion concentrations and with different degrees of purity of the sample. It is in no way indicative of a critical equilibrium temperature between the sol and gel forms, but is rather only a point on a continuous curve. This may be expressed by the equation:

$$\eta_{pH} = K / f(T),$$

where η_{pH} is the viscosity at equilibrium at any given pH, $f\ (T)$ is some function of the temperature, and K is a constant. On account of the length of time required to attain equilibrium, and the difficulty of eliminating completely all other influences as hydrolysis due to the prolonged action of water, electrolytes, or bacteria, the exact measurement of η_{pH} is uncertain, except where the conditions have been met for existence of an equilibrium *immediately*. This is the condition encountered where that temperature is obtained at which no change in viscosity with time is observed.

The idea of a gradual rather than an abrupt change on passing from the sol to the gel form is further indicated by the finding of Walpole[68] that the refractive index of a gelatin-water system is a linear function of the concentration, and if plotted against the temperature shows no discontinuity at any point between the liquid sol and the rigid gel. And McBain[69] has reported that the sol and gel of soaps differ only through the mechanical rigidity and elasticity of the gel form.

The writer[70] has shown that the gel consistency is proportional to the undegraded protein present in a gelatin or glue. It follows, therefore, that the unhydrolyzed gelatin possesses a much larger water-absorbing capacity than the proteoses or peptones. It was also pointed out that the viscosity varied apparently with the size of the colloid aggregate in the solution. The present theory demands that viscosity vary with the degree of water absorption (measured by the rigidity of the gel) and with the size (length) and number of the colloid fibrils (measured by the elasticity of the gel),[71] and also, of course, with the concentration of the solution. The " melting point " was shown[72] to be determined by the protein content and was found to give a " grading " lying between that resulting from measurements of gel strength and of viscosity at high temperature (60° C.). Since it has been indicated[73] that " melting point " is in reality only a transitional period between the sol and gel forms, and that the transition involves only a change in the water-absorbing capacity and the length and number of the colloid molecule-threads, it follows if the above is true that any measure of " melting point " will indicate a resultant between the effects of hydration or water absorption and of length or number of threads, or, differently expressed, a resultant between gel strength and viscosity at high temperature, which is exactly in conformance with the data reported in an early paper.

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[68] G. S. Walpole: *Kolloid-Z.*, **13** (1913), 241.

[69] M. E. Laing and J. W. McBain: *J. Chem. Soc.*, **117** (1920), 1506.

[70] R. H. Bogue: *Chem. Met. Eng.*, **23** (1920), 105.

[71] See Apparatus of S. E. Sheppard: *J. Ind. Eng. Chem.*, **12** (1920), 1007.

[72] R. H. Bogue: *J. Ind. Eng. Chem.*, **14** (1922), 435.

[73] R. H. Bogue: *J. Am. Chem. Soc.*, on press.

Fischer[74] is of the opinion that "the phenomena of hydration (swelling) and of 'solution' while frequently associated are essentially different. Hydration is to be regarded as a chance through which the protein enters into physico-chemical combination with the solvent (water); 'solution,' as an increase in the degree of dispersion of the colloid." This is in satisfactory agreement with the ideas expressed above, for although we do not consider that a true solution may exist at low temperatures on account of the heavy hydration or water absorption, yet the change in a jelly upon conversion to a liquid seems to involve a disintegration of the colloid aggregates (increase in degree of dispersion) as well as lessening in the degree of hydration or water absorption.

The recent work of McBain and his collaborators[75] on the structure of the sol, gel, and curd of soaps is of especial interest and is in agreement with the theory outlined. They report that in soaps "the colloidal particles in the sol and gel are the same, but whereas in the former they are independent, in a fully formed gel they stick together, probably to form a filamentous structure." They add further that "the sol and gel differ only through the mechanical rigidity and elasticity of the gel form." That is precisely what would follow in gelatin sol and gel from the postulations made above, and is further indication of the gradual nature of the changes which obtain in the sol-gel equilibrium. They state as their belief that a filamentous structure is the general characteristic of soap gels as distinguished from sols. They regard these filaments, however, as normally amicroscopic in size, while in the curds a probably crystalline formation is produced. In gelatin systems the curd or crystalline condition is not known. Harrison,[76] however, reports that he has obtained ultramicroscopic photographs of gelatin and cellulose gels which showed them to consist apparently of "minute portions joined together in a somewhat irregular manner."

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[74] Martin Fischer and W. D. Coffman: *J. Am. Chem. Soc.*, 40 (1918), 304; Martin Fischer: "Soaps and Proteins," New York (1921), 219.

[75] Mary E. Laing and J. W. McBain: *J. Chem. Soc.*, 117 (1920), 1506; W. F. Drake, J. W. McBain, and C. S. Salmon: *Proc. Roy. Soc.* London, A 98 (1921), 395.

[76] W. Harrison: *Cf.* Ref. 40, p. 57.

Barratt[77] has accepted the fibrillar structure theory as representing most adequately the properties of elastic gels, and reports that ultramicroscopic examination, when it reveals any structure at all, shows the gel to consist "not of liquid droplets enclosed by (solid) septa, as the honeycomb theory requires, but of a mass of intersecting fibrils, which run perfectly straight, and are united at their points of intersection." He concludes that "the real structure of these gels is a fibrillary network, at first amicroscopic and later becoming ultramicroscopic."

A gradual and regular change in properties accompanying the transformation of the sol to the gel or the gel to the sol also supports the theory of structure that has been set forth. This gradual and regular change is indicated by the viscosity-plasticity studies described; by the finding of Walpole[78] that the refractive index of a gelatin-water system is a linear function of the concentration, and when plotted against the temperature no break occurs in the region of gelation; by the conclusion of McBain[79] that the sol and gel forms of soap differ only in the formation of a filamentous structure which accounts for the different properties of the latter; by the reports of C. R. Smith[80] that mutarotation exists between the temperature 15° and 30° C.; by the demonstration of Arrhenius[81] that the conductivity of salt-gelatin-water systems was the same in the sol and the gel conditions; and by the findings of Thomas Graham[82] that the rate of diffusion in dilute gels was approximately the same as in pure aqueous solutions.

It is also of interest to note that dibenzoyl-*l*-cystine which has recently been described by Gortner,[83] and which is capable of forming an elastic gel at concentrations as low as 0.2 per cent., was also shown by an ultramicroscopic examination to consist, in the gel condition, of a fibrillar structure.

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[77] J. O. W. Barratt: *Biochem. J.*, **14** (1920), 189, *Cf.* Ref. 40, p. 49.

[78] G. S. Walpole: *Kolloid-Z.*, **13** (1913), 241.

[79] M. E. Laing and G. W. McBain: *Loc. cit.*

[80] C. R. Smith: *J. Am. Chem. Soc.*, **41** (1919), 146; *J. Ind. Eng. Chem.*, **12** (1920), 878.

[81] S. Arrhenius: *Ofvers. Stockh. Akad.* (1885), No. 6, 121.

[82] Thomas Graham: *Phil. Trans. Roy. Soc.*, 1864.

[83] R. A. Gortner: *J. Am. Chem. Soc.*, **43** (191), 2199.

Experiments upon the influence of H-ion concentration and of inorganic ions on the swelling, viscosity, jelly consistency, foam, turbidity, and alcohol number were shown to give data which supports the theory presented. The occlusion theory of Loeb,[84] which has already been described, is also found to be in harmony with the views presented.

Notwithstanding the very considerable progress that has been made in the last ten years in the fields of the chemistry and technology of gelatin and glue, there remains much for the immediate future to accomplish. A beginning has been made which will insure a momentum to this branch of chemistry for a long period to come, but problems of importance await solution at every turn, and if there be competent chemists who are searching for interesting research, we invite them to a consideration of gelatin and glue.

The Disappearance of Gas in the Electric Discharge. Research Staff of the General Electric Company, Ltd., London. (*Phil. Mag.*, May, 1922.)—Hydrogen and nitrogen behave in very nearly the same way in respect to disappearance in the electric discharge. In the case of these two gases when phosphorus is present the following conclusions are reached:

1. "The nature of the discharge has little direct effect upon the amount of gas absorbed."

2. "The form of vessel is important only in so far as it affects the area of the wall exposed to the discharge."

3. "The pressure of the gas during absorption has no affect within wide limits on the amount absorbed."

4. There is a very irregular connection between the amount of phosphorus present and the amount of gas absorbed. In general the two increase together, but not always.

5. The condition of the glass walls of the vessel makes no difference, but the deposit of certain salts or of tungsten on the walls greatly increases the absorption.

A suggested explanation ascribes the absorption to an electrically polarized solid layer on the surface, in one case of phosphorus, in another of the salts. When negatively charged ions approach the surface they are attracted and held fast. In the case of absorption by glass alone it may be that its surface layer is polarized by the discharge. It will be noted that much more is known about the phenomenon than about its causes. G. F. S.

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[84] Jacques Loeb: *J. Gen. Physiol.*, 3 (1921), 827; 4 (1921), 73. 97.

A SOURCE OF LIGHT GIVING A CONTINUOUS SPECTRUM IN THE ULTRA-VIOLET.*

BY

W. H. FULWEILER AND JAMES BARNES.

Members of the Institute.

In our observations on the ultra-violet absorption spectra of some hydrocarbons and petroleum oils, we have used a source of light which has given such satisfactory results that a brief description of it may interest others who are working in this field of spectroscopy.

The source of light which has been used very extensively by investigators is the condensed spark between electrodes of various metals and their mixtures. While the manipulation of this source is very simple, it has the great disadvantage that its spectra consists of many bright lines superimposed on a more or less continuous background.

When using this source of illumination it is difficult to determine the edges of absorption bands when they are close to or coincident with a bright line so that it is frequently necessary to use more than one metal in order to eliminate this difficulty.

It is obvious that a source of illumination that would give a continuous spectrum in the ultra-violet would not only be very much more convenient but should enable the absorption bands to be more accurately located.

Grebe [1] seems to have been one of the first to use a continuous source of illumination in the ultra-violet for spectroscopic work. In his apparatus, the spark was passed between aluminum electrodes under flowing water. The aluminum electrodes give off a considerable amount of oxide and wear away quite rapidly so that they must be continually adjusted.

Howe [2] employed the high-frequency oscillations set up by means of a Tesla coil to produce a spark between aluminum electrodes placed under distilled water, and he states that this source gives a continuous spectrum that extends with long exposures to 2100 A. U.

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* Communicated by the Authors.

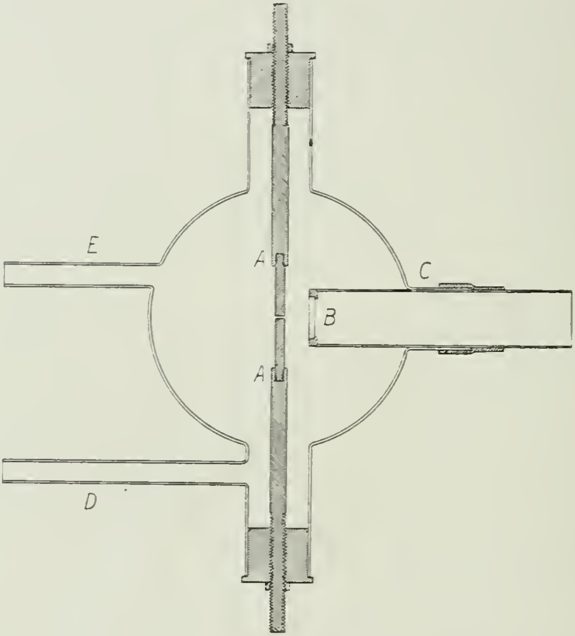
[1] *Zeitschr. f. wiss. Photo.*, 3, 376, 1905.

[2] *Phys. Rev.*, 8, 674, 1916.

Strachan[3] has used high-frequency oscillations with a Tesla coil and brass electrodes under water. Using from 4 to 6 kilowatts in the primary of the transformer, he secured a very satisfactory continuous spectrum extending to 2200 A. U.

After trying the spark with a number of alloys we set up apparatus similar to that used by Howe, but did not secure results desired. After making a number of modifications, the principal one being the omission of the Tesla coil, we finally secured a set-up which gave very satisfactory results.

Fig. 1.



Method.—The final modification of the apparatus is shown in Fig. 1.

The electrodes A consisted of tungsten rods 3.5 mm. in diameter. These are mounted in brass rods which screwed into solid rubber stoppers. The stoppers were sealed with hard wax on the side tubes of a pyrex glass bulb of about 500 c.c. capacity. By means of the threads on the brass rods the position of the spark gap relative to the quartz window B, and also the length of the gap could be easily adjusted. We found under the electrical conditions used that a spark length of about ½ mm. was the most satisfactory. The quartz plate B, 16.5 mm. diameter, was fixed by washers and screw cap to the end of a brass tube which slipped through the side tube C of the vessel and was held in position by a rubber tube. The spark gap was about 1 cm. from the window and about 2 cm. below the surface of the water which flowed in through the tube D and out at E.

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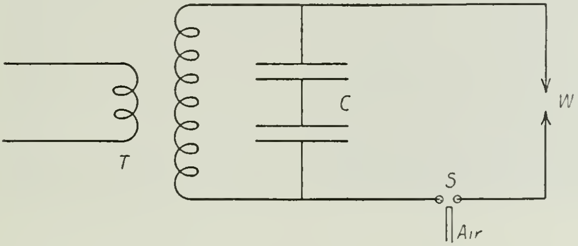
[3] E. K. Strachan, private communication.

For the production of the spark we employed a G. E. X-ray transformer, type K, using 15 amperes from the 110 volt A. C. mains on the primary coil. A mercury interrupter which made and broke a D. C. current about 120 times a second was also employed. For capacity, two Leyden jars of about .001 m.f.d. each were used. A zinc spark gap upon which a blast of air was directed was placed in series with the tungsten spark. Fig. 2 shows this electrical circuit where T is the transformer; C, the capacity; S, the external spark gap and W, the tungsten spark.

FIG. 2.

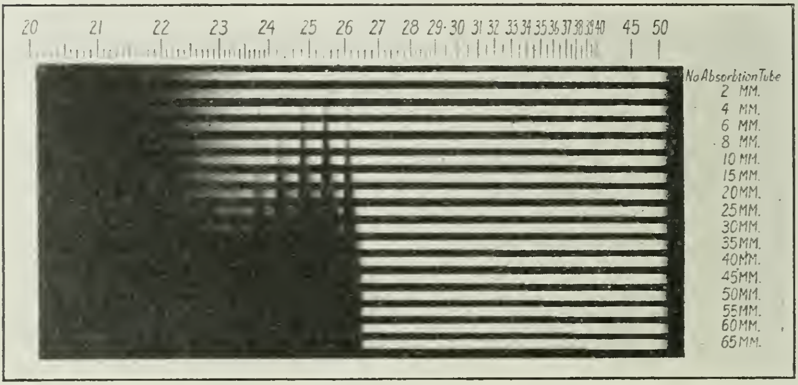


The choice of tungsten for the electrodes was made after a careful trial of aluminum, brass, iron, nickel, carbon and molybdenum. The tungsten gave more light in the shorter wavelengths and required very much less adjustment.

Using 1.6 k.w. in the primary of the transformer, the tungsten electrodes disintegrated very slowly compared with aluminum poles used under exactly the same conditions. The spark length had rarely to be adjusted during a complete set of observations as for example the set shown on Fig. 3.

Results.—As illustrating the results obtained with this source of illumination, we have reproduced on Fig. 3, a positive from one of our negatives showing the absorption bands of 0.1 per cent. solution of benzene in ethyl alcohol. The lengths of solution used are indicated on the side of the plate. It is unfortunate that reproduction does not do justice to the very fine detail that is present in the original plate. This photograph is taken with a Hilger quartz spectrograph, type E-2, using a slit of 0.05 millimetres with two minute exposure on a Seeds 23 plate. One and six-tenths k.w. were used in the primary of the transformer.

Fig. 3.



The top exposure in Fig. 3 with no absorption tube indicates the uniformity of the illumination. In the original negative the spectrum extends to 2050 A. U. In connection with the absorption bands of benzene, the original negative shows eleven bands, some of these are lost, however, in the reproduction.

Chemical Laboratory,
The United Gas Improvement Company,
Philadelphia, May 3, 1922.

Soy Bean Oil.—W. B. Smith (*Jour. Ind. Eng. Chem.*, 1922, xiv, 530–531) has analyzed several samples of soy bean oil. He finds that an oil with an iodine number of 134 has approximately the following composition: Linolenic acid, 2 to 3 per cent.; linolic acid, 55 to 57 per cent.; oleic acid, 26 to 27 per cent.; saturated acids, 9 to 10 per cent. J. S. H.

THE RESOLUTION OF THE Kα DOUBLET IN THE POWDER METHOD OF X-RAY CRYSTAL ANALYSIS.*

BY

L. W. McKEEHAN, PH.D.

Research Physicist, Engineering Department, Western Electric Company.

IN the powder method of X-ray crystal analysis, suitably oriented crystals large enough to give separately distinguishable spots on the photographic film reflect the two wave-lengths of the Kα doublet—Kα_1 and Kα_2—at slightly different angles, so that these spots are also doublets.

Using a copper anti-cathode, W. Gerlach[1] reported that the separation of such doublets was only about half of the value which he expected from the known values of the wave-lengths. As I mentioned in a recent paper,[2] the positions of double spots in my photographs taken with a molybdenum anti-cathode were in rough agreement with the equations

$$\lambda_1 = 2d \sin \theta_1 \qquad (1)$$

$$\lambda_2 = 2d \sin \theta_2 \qquad (2)$$

wherein $2\theta_1$ and $2\theta_2$ are the angles which lines joining the centre of the sample to the centres of the spots make with a line joining the centre of the source with the centre of the sample.

In a recent note, F. Kirchner[3] has explained the small values for spot separations obtained by Gerlach as theoretically justified, and Gerlach[4] has recalculated the values of wave-length difference, Kα_2 − Kα_1, from his measured separations, getting very good agreement with experimental and theoretical results for copper and nickel radiators.

This leaves my results apparently out of line with both theory and experiment, but it is quite easy to show that there is no real contradiction, both results agreeing with a complete theory of the phenomenon.

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* Communicated by Brigadier General John J. Carty, D. Eng., Associate Editor.

[1] W. Gerlach, *Phys. ZS.*, 22, 557–559 (1921).

[2] L. W. McKeehan, FRANK. INST. JOURN., 193, 231–242 (1922).

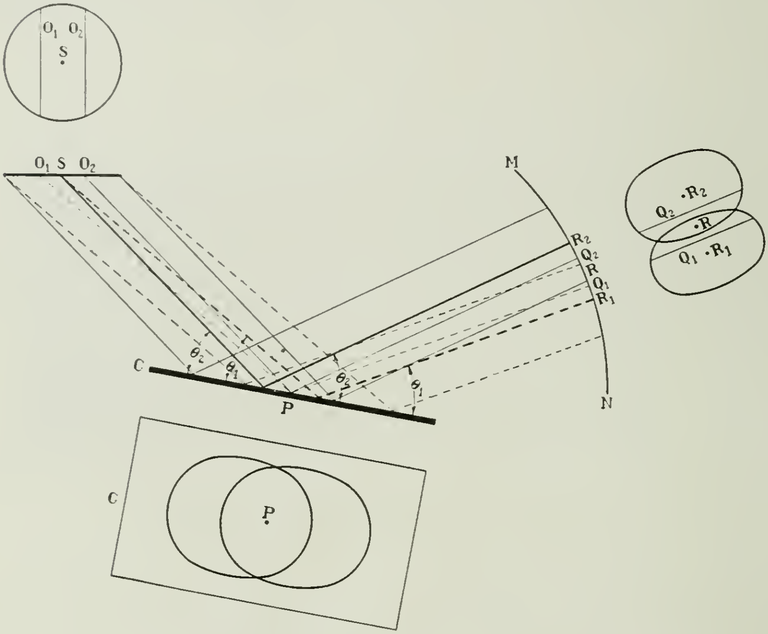
[3] F. Kirchner, *Phys. ZS.*, 23, 114 (1922).

[4] W. Gerlach, *Phys. ZS.*, 23, 114-120 (1922).

In Fig. 1 let S be a plane source of any finite extent giving X-rays of two wave-lengths, λ_1 and λ_2 ($\lambda_2 > \lambda_1$). Let C be a group of crystal lattice-planes with primitive interval d. There will be two reflected beams, as shown, where equations (1) and (2) determine the values of θ_1 and θ_2.

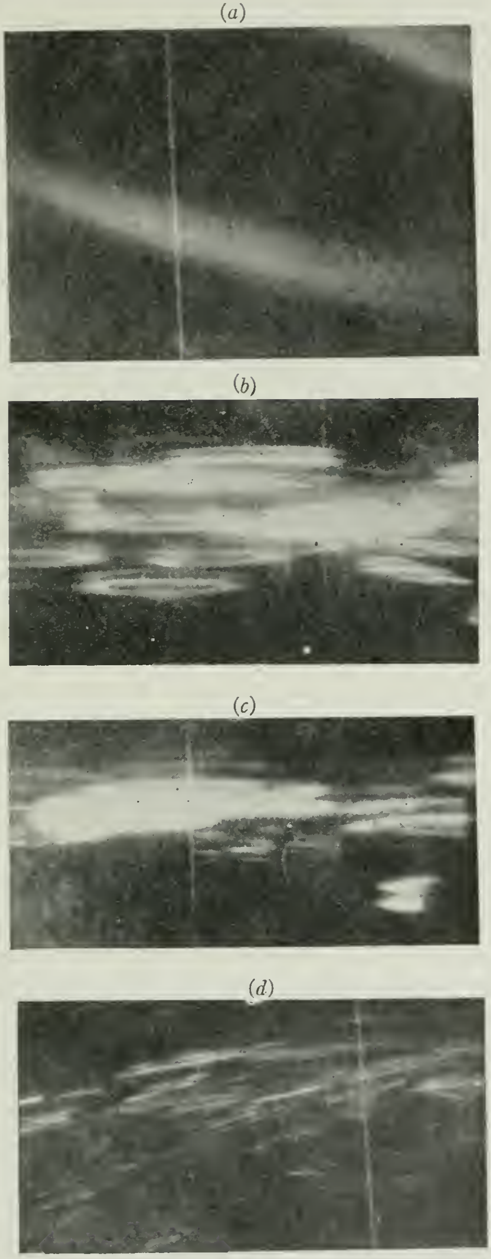
If the crystal is of unlimited area each point of the source will give a complete circular cone of reflected rays with its apex at the ordinary mirror image of the chosen point in the plane C, and cutting the film MN in a curved line. With long crystals of tungsten, such traces have been obtained about 2 cm. long and showing a slight convexity on the less deflected side, as they should, considering the actual shape of MN, which was a circular cylinder centered at P. An enlarged reproduction of such traces is given in Fig. 2 (a). The double character of these long traces is evident, but they are not well enough defined for accurate measurement of the separation.

Fig. 1.



Smaller crystals give patterns on the film which show clearly the distribution of intensity among the points of the source which,

FIG. 2.



Actual width of fields is 2.0 cm.

by pin-hole photographs was found to be a brilliant annulus with a relatively non-emitting centre. The two pairs of parallel projections indicated in Fig. 1 give rise in the film to two very nearly similar elliptic bands, the ratio of the major to the minor diameter of each ellipse being about 8 and the major diameter being about 0.6 cm., the same as the diameter of the circular source. A pair of such ellipses is shown in Fig. 2 (*b*).

These ellipses are not sharply defined except near the ends of their minor axes, because of the width of the crystal. The wider the crystal the longer is the trace of the cone of reflected rays which were emitted at a point on the source, and the "image" of the source is built up by the superposition of these parallel lines of limited length exactly as a real image in any optical system is built up by the superposition of the diffraction patterns due to the points of the source. An additional cause of blurring is the thickness of the crystal perpendicular to the reflecting planes, but this was not serious with the thin sheets of metal which I found most convenient for other reasons.[5]

Inspection of Fig. 1 shows that the arc length R_1R_2 between the centres of the two elliptical spots is given by

$$R_1 R_2 = (SP + PR)(\theta_2 - \theta_1) \ .$$

In the actual apparatus SP and PR were nearly equal, so that to a first approximation

$$R_1 R_2 = 2\,PR\,(\theta_2 - \theta_1) \ .$$

Crystals too small to intercept both of the reflectable beams in their entirety will give rise to defective ellipses, one or both being cut off by lines due to the boundaries of the crystal, so that the ellipses may be cut off by lines in any position with respect to the axes of the ellipse. An example of such defective ellipses is given in Fig. 2 (*c*). It is clear that with the disposition shown in Fig. 1 it would be possible to have one ellipse complete and the other reduced to a narrow arc on the side nearest to the unaffected spot. If the beams do not overlap on C one spot of the pair may be wholly absent.

Carrying the reduction in size of the reflecting surface still farther, a very small area at P, in the region common to the two beams, will reflect only rays from O_1 and O_2, to Q_1 and Q_2, respectively, so that the two ellipses are now represented simply by two chords, that is, by two very narrow parallel lines on the film. This is the case obtained by Gerlach, and occurs in my experiments with metals where special heat treatment has permitted the formation of very small crystals free from strain. A region showing several such pairs of lines is shown in Fig. 2 (*d*). An area outside the region common to the two beams cannot give rise to two lines of this sort, so that single lines are also of frequent occurrence.

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[5] L. W. McKeehan, *Loc. cit.*

The arc length Q_1Q_2 between the lines due to reflection from the same tiny crystal is given by

$$Q_1Q_2 = PR\,(\theta_2 - \theta_1)\,,$$

half the approximate value found above for R_1R_2. If differences in wave-length are to be determined this may be put in the rigorous form

$$\lambda_2 - \lambda_1 = \frac{\lambda_2 + \lambda_1}{2} \cot \frac{\theta_2 + \theta_1}{2} \tan \frac{\theta_2 - \theta_1}{2}$$

or for small values of $(\theta_2 - \theta_1)$

$$\lambda_2 - \lambda_1 = \frac{\lambda_2 + \lambda_1}{2} \cdot \frac{Q_1Q_2}{PR} \cot \frac{\theta_2 + \theta_1}{2}\,.$$

In the case of molybdenum, Duane[6] gives

$$\lambda_2 = K\alpha_2 = (0.71212 \pm 8) \times 10^{-8} \text{ cm.}$$

$$\lambda_1 = K\alpha_1 = (0.70783 \pm 7) \times 10^{-8} \text{ cm.}$$

so that $$\lambda_2 - \lambda_1 = (4.29 \pm 11) \times 10^{-11} \text{ cm.}$$

My measurements upon a single photograph where many sharply defined pairs of lines occurred gave

$$\lambda_2 - \lambda_1 = (4.36 \pm 5) \times 10^{-11} \text{ cm.}$$

in satisfactory agreement with Duane's value. Gerlach's values computed in this way agree equally well with previously published values of comparable accuracy for copper and nickel.

SUMMARY.

Double spots due to reflection of two nearly equal wave-lengths by the same crystal may be of two kinds.

(1) Fine parallel lines are due to reflection of rays from different parts of the source by a very small crystal. The separa-

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[6] W. Duane, *Nat. Res. Counc. Bull.*, 1, 383–408 (1920).

tion of such lines depends only upon the difference in wave-length, the mean wave-length, and the mean of the observed angles of reflection. They are excellent objects under the microscope and give an accurate method for determining small differences in wave-length.

(2) Projected images of the whole source are due to reflection of rays from each point of the source at different points in the crystal. The separation of such images depends upon the difference in wave-length, the mean wave-length, the mean of the observed angles of reflection and upon the ratio of the whole path-length of the rays to the path-length after reflection. In the usual arrangement spots of the second kind are about twice as far apart as spots of the first kind.

Duane's value for the wave-length difference of the Kα doublet of molybdenum has been checked by measurements on spots of the first kind.

Research Laboratories of the
American Telephone and Telegraph Company
and the Western Electric Company, Inc.
March 17, 1922.

Facts About Asbestos. (*Engineering World,* June, 1922, p. 371.)—The art of weaving the mineral fibre in asbestos, which is ordinarily indestructible, was rediscovered at a comparatively late period of civilization. Woven asbestos was used in the ancient pyre to preserve the royal ashes. Charlemagne is said to have had a tablecloth made of asbestos and to have cleaned it by throwing it into the fire, which consumed the dirt, thus illustrating in a spectacular manner one of the most valuable properties of this material.

The fibre of the best grade of asbestos is beautiful and silky and has great flexibility, elasticity and tensile strength. It can be spun into thread so fine as to run 225 yards to the ounce, and as it is incombustible as well as a non-conductor of heat and electricity and resists the action of most ordinary acids, its field of use is large. The possible applications of asbestos are far from fully appreciated, not only by the general public but by manufacturers who are in search of material for special uses to which asbestos may well be applied. Perhaps it is most generally used to make fireproof cloth for theatre curtains. It has been used also for making firemen's clothing. Everywhere in cold countries it is extensively employed for covering furnaces, boilers and pipes to prevent loss of heat. Asbestos is a good insulator. R.

NOTES FROM THE U. S. BUREAU OF STANDARDS.*

THERMAL EXPANSION OF A FEW STEELS.[1]

By Wilmer Souder and Peter Hidnert.

[ABSTRACT.]

THERMAL expansion data on 28 samples of iron and steel are given. One sample of vacuum electrolytic iron and one of gray cast-iron are included. A specimen of hardened steel has been tested to show the dimensional changes incident to heat treatment or drawing. Twenty-two curves and a two-page table are used to summarize the results.

The average expansion of the specimen of electrolytic iron is 12.0×10^{-6} for the range 25 to 100° C.

For 25 steels:

11.2×10^{-6} for the range 25 to 100° C.
and 14.2×10^{-6} for the range 25 to 600° C.

Above the critical region the values usually jump to approximately 23×10^{-6}.

The values on cooling are not very different from those on heating; the transformation regions are displaced as usual.

The contraction and expansion reversals within the critical regions vary from a few microns per metre, if any at all, for a 3.7 per cent. silicon steel, to almost 2000 microns per metre for a 1.2 per cent. chrome steel (C, 0.35; Cr., 1.17; V, 0.14).

The critical region was found to extend over a temperature interval of from less than 6° C. for electrolytic iron to something over 100° C. for a special 1.1 per cent. manganese steel. These differences in dimensional changes and extent of critical region are suggested as a means for determining the tendency toward cracking or warping when parts of specimens are quenched at unequal rates. This rate is always different, depending upon the size, shape, etc.

The completion of the transformations on heating and the beginning on cooling were found to be separated by varying amounts, from 10 to 100° C., approximately. Since quenching

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* Communicated by the Director.

[1] Scientific Papers No. 433.

temperatures are usually determined from heating curves rather than cooling curves, the question is raised as to the possibility of errors approaching 100° C. in these quenching temperatures.

The length changes of a piece of hardened steel indicate a small shrinkage when heated above 50° C. This continues for temperatures up to 100° C. After a repeated heating to 100° C. and holding at this temperature for a few hours no further shrinkage was observed, even upon carrying the temperature to 200° C. Upon heating to 250° C. a second shrinkage began and continued to approximately 375° C.

The specimen of cast-iron showed irregularities and considerable permanent growth upon heating, the growth being especially rapid at temperatures above 650° C.

A brief review of some of the previous work on expansion is included.

METALLOGRAPHIC ETCHING REAGENTS; II, FOR COPPER ALLOYS, NICKEL, AND THE ALPHA ALLOYS OF NICKEL.[2]

By H. S. Rawdor and Marjorie G. Lorentz.

[ABSTRACT.]

THIS article constitutes the second part of the general investigation of metallographic etching reagents in progress at this Bureau. It is closely related to the one already published on copper in the methods employed and results obtained. The following materials were used: Copper alloys, including brasses, bronze and aluminum bronze; nickel and the α alloys of nickel, monel metal, cupro-nickel and nickel brass.

Experimental results are given to show the importance of films in producing contrast in etching. Oxide and sulphide films were used, and it was shown by separating the etching and the filming operations that films varying in thickness on the individual crystals are produced by certain reagents and give rise to "contrast." The better understood method for producing contrast by a differential roughening of the crystals upon etching is also illustrated.

The α copper alloys closely resemble copper in their general behavior upon etching and in the character of the results produced. The addition of tin to brass appears to render it slightly less respon-

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[2] Scientific Papers No. 435.

sive to etching reagents than the same alloy without tin; aluminum bronze in the rolled condition was the most unsatisfactory of the copper alloys examined to etch. A series of copper-zinc alloys representative of all the types of structure in this series was examined. The alloys rich in zinc resemble this metal in their etching characteristics more than they do the copper-rich alloys, in that highly oxidizing etching reagents do not appear to be necessary for the successful etching of the alloy.

Nickel, particularly when of high purity, is etched with considerable difficulty. Oxidizing acids, such as nitric, and acids to which strong oxidizers had been added were found effective for a quick etching. For producing a contrast etch-pattern with freedom from pitting a long immersion in concentrated hydrochloric acid was found to give excellent results.

Of the α nickel alloys examined, monel metal and cupro-nickel were found to resemble nickel in their etching properties, though they etched more readily. The nickel brasses (nickel silver) resemble the α copper alloys in many respects and were readily etched by the reagents used for the brasses and bronzes.

The copper alloys behave very similarly to copper in their behavior toward etching reagents through which oxygen was bubbled. They were readily etched by reagents, ammoniacal, acid, or neutral, which otherwise would have but slight effect upon them, provided a stream of oxygen was passed through the solution while the specimen was immersed. Nickel was found not to be effected materially in its rate of etching by the use of oxygen gas except in the degree of pitting produced in some specimens. Cupro-nickel and monel metal resemble nickel in this respect, and the nickel brasses are somewhat like the copper alloys. They respond to the ammoniacal solutions containing oxygen though not to acid solutions and oxygen.

THE SOLUBILITY OF DEXTROSE IN WATER.[3]

By Richard F. Jackson and Clara Gillis Silsbee.

[ABSTRACT.]

THE solubilities of dextrose, which are of fundamental importance in controlling the process of manufacture, have been determined over a range of temperatures extending to 90° C. The

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[3] Scientific Papers No. 437.

respective solid phases were agitated in contact with their aqueous solutions in containers under the water of a thermostat until saturation was attained. The viscous saturated solution was separated from the crystals by an asbestos pressure filter constructed for the purpose. Solutions were analyzed by densimetric and polarimetric measurements.

Three solid phases are capable of existence below 90° C., namely, ice, α-dextrose monohydrate, and anhydrous α-dextrose. The freezing point curve, computed from existing data, intersects the solubility curve of dextrose hydrate at −5.3° C. and at a concentration of 31.75 per cent. dextrose. This intersection is therefore the cryohydric point.

α-dextrose with one molecule of water of crystallization is the stable phase between −5.3° C. and 50° C. It occurs in the form of minute lustrous plates which under carefully regulated conditions are capable of growth to six or more mm. in length. The solubility shows a very high temperature coefficient. Thus at 0.5° C., 100 g. of water dissolve 54.32 g.; at 30° C., 120.5 g.; and at 50° C., 243.8 g. of dextrose (calculated as anhydrous sugar).

The hydrate shows a melting point of about 83° C., the exact temperature being apparently uncertain and unreproducible. The solubility curve, however, can not by any manner of extrapolation be made to pass through this temperature at a concentration of 90.9 per cent. (the composition of the crystals). The solubility measurements were, however, shown to be compatible with the observed melting point on the theory that β-dextrose is present in the saturated solution, but absent during a melting point determination. By an approximate calculation of the solubilities of α-dextrose in solutions containing only α-dextrose, a solubility curve was obtained which was consistent with the observed melting point of the crystals.

The transition from α-dextrose hydrate to the anhydrous form occurs at 50° C.

Above the transition point the anhydrous form is stable and its solubility rises linearly, but with relatively small temperature coefficient. At 50° C. the solubility is 70.91 per cent.; at 70.2° C., 78.23 per cent.; and at 90.8° C., 84.9 per cent. The anhydrous form is capable of existing in metastable equilibrium below the transition point. It was found to be feasible to make approximate solubility measurements down to 28° C.

SENSITOMETRY OF PHOTOGRAPHIC EMULSIONS AND A A SURVEY OF THE CHARACTERISTICS OF PLATES AND FILMS OF AMERICAN MANUFACTURE.[4]

By Raymond Davis and F. M. Walters, Jr.

[abstract.]

This article is the result of a survey of about 90 different brands of photographic plates. In this survey the speed, developing characteristics, color sensitiveness, filter factors, and scale of the plates were investigated.

The introductory part deals in a general way with: The preparation and classification of emulsions; photographic filters: the relation between exposure of the photographic plate and the resulting density; the effect of time of development on contrast; speed and inertia; scale and latitude; other methods of measuring plate speeds; effect of the presence of bromide in the emulsion; and the general methods of development in use.

The second part is devoted to the apparatus and methods employed in the investigation. For obtaining the exposure density curves as well as the color sensitiveness of the emulsions a light source having both standard intensity and standard composition is necessary. For this the Bureau has chosen one having the composition of average noon sunlight at Washington and an intensity at the test plate of one candle metre—a Mazda C automobile headlight, operating on approximately 2.4 amps., combined with a suitable filtering screen.

The sensitometer, special design, was of the sector-disc type, exposing each of nine successive areas on a given plate, for double the time of the preceding area. With an ideal emulsion the brightness of a given field of light viewed through these different areas of the developed plate would be reduced by equal steps, passing from the area of least to that of greatest exposure. The instrument is described in Patent No. 1,382,272, R. Davis, sensitometer for testing plates and films—dedicated to the public. The exposures chosen were such that false values introduced by the intermittency of the light were negligible. For measuring the densities of the exposed plates a Martens photometer mounted in a specially designed illumination box was used. The plates were developed in silver-plated cans immersed in a thermostated bath.

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[4] Scientific Papers, No. 439.

For investigating the color sensitivity two methods were employed: That of photographing the spectrum to reveal the region of sensitiveness; and that of measuring the filter factors to determine how one plate compares with another when different filters are used. For obtaining the spectrograms, a transmission diffraction grating was used, giving a normal spectrum, the red part of which passed through a yellow screen to cut out the violet rays of the next higher order. Between the source, giving uniform illumination of the slit, and the slit, a rotating sector was interposed which produced a geometrically decreasing illumination from bottom to top of the resulting spectrum. The rectangular area which the spectrum covers on the photographic plate shows, when the exposed plate has been developed, a dark peak wherever the plate is sensitive to the corresponding color. The results being qualitative rather than quantitative the source of light—a tungsten filament—was not adjusted to the composition of sunlight.

The filter factor apparatus was designed to reduce the intensity of the undimmed white light on the plate by a measurable amount until it gives, for the same exposure time, the same darkening effect as the light which passes through the filter. The ratio of the intensity used on the filter side to that used on the undimmed side is the filter factor of the given plate for the given filter. For this work, to give filter factors for outdoor purposes, a corrected source similar to that used with the sensitometer was employed. The reliability of the filter factors thus obtained is illustrated by comparative photographs.

The third part gives data obtained from practically all brands of emulsions made in the United States—the trade names of the emulsions being omitted.

THE REDWOOD VISCOSIMETER.[5]

By Winslow H. Herschel.

[ABSTRACT.]

THE Redwood viscosimeter was selected for calibration because it is standard in England and because there appeared to be some doubt as to whether or not the instrumental constants varied with the temperature. It is stated that the instrument is so adjusted that the time of flow for 50 cubic centimetres of rape seed oil at

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[5] Technologic Papers No. 210.

60° F. (15.6° C.) is 535 seconds, but this oil is so variable in viscosity that the statement is of little value in determining the equation of the instrument. The standard dimensions are also inadequate as published.

By calibration with oils whose viscosity had been determined in a capillary tube instrument, the equation was obtained

$$\text{kinematic viscosity} - .00260\,t - \underline{1.88}$$

where t is the time of flow in seconds.

In the course of the work two common errors in viscosimetry were investigated with the following results:

1. It was found that the error due to inaccuracy in the Meissner formula for average head was negligible in ordinary work.

2. The error due to cooling of the oil after leaving the outlet tube may be neglected at low temperatures, but should be corrected at temperatures near the boiling point of water. Diagrams were prepared to assist in making this correction.

The tests showed that any variation in instrumental constants at different temperatures is probably due to the last mentioned error, so that viscosimeters may be calibrated at any convenient temperature, varying the viscosity either by change of temperature or by blending. Outlet tubes may be made of any suitable durable and non-corrosive material, without regard to its coefficient of expansion. Thus the time ratios of the Redwood, Saybolt Universal, and Engler viscosimeters were found to be independent of temperature, although the outlet tubes of instruments of the first type are made of agate, and tubes of the other instruments are made of metal.

RADIATORS FOR AIRCRAFT ENGINES.[6]

By S. R. Parsons and D. R. Harper, 3rd.

[ABSTRACT.]

IN a technological paper bearing the above title, the National Bureau of Standards communicates much material which it is hoped will prove of value to the automotive industry, as well as of interest to physicists and engineers generally. The paper describes the laboratory investigations relating to aircraft engine radiators which were conducted by the Bureau of Standards during the

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[6] Technologic Paper No. 211.

World War and in the two years immediately succeeding it. Individual reports covering many phases of the subject have been published previously in the technical series of the National Advisory Committee for Aeronautics and in scientific and engineering journals. These reports, however, lack the systematic coördination, uniform terminology, and unified mathematical treatment which should characterize a handbook on the subject. Moreover, the problems, which were investigated first because of their greater importance and which were the subjects of the reports published earliest, are for that reason not so well covered as is now possible because the later work threw much additional light upon matters not settled up to the time of publication of the early reports. Accordingly, the present paper is much more than a reprint of earlier reports, being a complete revision and recompilation of the material available.

The special investigations reported included development of the methods of measuring air flow in radiator tubes; experiments upon the effect of nature of surface upon air flow and upon heat dissipation from the surface of metal tubes to a high velocity air stream; experiments to ascertain the degree of turbulence in the air tubes of a radiator core; mapping of temperature distribution, axially and transversely, in the air tubes of radiator cores. In addition to recording these special investigations the paper contains a full description of laboratory methods and instruments for those tests of radiator cores properly made in the laboratory, both of physical properties and geometrical characteristics such as size and shape of air tubes and of water tubes.

The work included laboratory measurements of cooling power, head resistance, and geometrical characteristics of over one hundred types of radiator core. Performance characteristics of 66 types of core are given in graphical form. General conclusions from these measurements and from the special laboratory experiments mentioned above are incorporated into an exposition of the fundamental relations between the conditions under which a radiator operates, its characteristics of form and construction, and the properties which describe its performance. This portion of the designer's field is by no means the whole, however, and the paper does not treat the important consideration of sturdiness, ease of construction and repair, cost, form of design imposed by the structure of the aircraft, etc.

Among the features of the paper may be mentioned empirical equations for relating heat dissipating power of a radiator to the air flow through the core, for computing the performance of a core of any depth from that of a core of exactly similar construction but different depth, for computing air flow through simple honeycomb cores for given flying speeds in an unobstructed position, and for computing heat dissipating power of such cores from their geometrical dimensions. The effectiveness of indirect cooling surface (cooling surface not backed by flowing water) is developed mathematically, reduced to a practical working equation, and applied to computation of optimum fin dimensions for given conditions. Also the equations of thermal conductivity are applied to produce a table showing temperature drop through metallic water tube walls of radiators of various wall thicknesses and material.

The effect upon heat dissipation of varying rate of water flow is considered in detail, also a comparison of methods of testing radiator cores calorimetrically, using superheated steam as a source of heat and using hot water as the source, a table being given which contains the essential steam data for computing results of a measurement made by the method first mentioned.

Many topics, treated briefly, have to do with such details of radiator performance as effect of yaw, slipstream mountings, wing radiators, shuttering, radiator requirements at altitude, and methods of computing performance at altitude from test data obtained under ground-level conditions. Experiments are described which investigated the effects of a partially streamlined casing enclosing a radiator. Experimental work upon a model fuselage nose radiator mounting showed clearly that for high speed flight the figure of merit of an unobstructed radiator and streamline nose is sufficiently above that of a nose installation to warrant careful study of the structural difficulties to be overcome in adopting such an arrangement.

TESTS OF STELLAR RADIOMETERS AND MEASURMENTS OF THE ENERGY DISTRIBUTION IN THE SPECTRA OF SIXTEEN STARS.[7]

By W. W. Coblentz.

[abstract.]

The object of the present investigation was (1) to test new stellar thermocouples, (2) to verify previous measurements of

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[7] Scientific Papers No. 438.

stellar radiation, (3) to measure the radiation intensities of bright stars in the region of 0 hours to 12 hours, in right ascension, not previously measured, and (4) to determine the feasibility of the method of obtaining the spectral energy distribution of stars by means of transmission screens which, either singly or in combination, are placed in front of the vacuum thermocouple.

By means of vacuum thermocouples, measurements were made on the total radiation intensities of thirteen bright stars not observed in 1914, thus completing the survey of the whole sky. A total of thirty celestrial objects were measured, including Venus and Mars.

By means of a series of transmission screens (of yellow and red glass, of water, and of a thick plate of quartz) wide spectral regions were isolated and the radiation intensities in the spectrum from 0.3μ to 0.43μ, 0.43μ to 0.6μ, 0.6μ to 1.4μ, 1.4μ to 4.1μ, and 4.1μ to 10μ were determined. In this manner the distribution of energy in the spectra of sixteen stars was determined, thus obtaining for the first time an insight into the radiation intensities in the complete spectrum of a star.

By means of these transmission screens it was found that in the Class B and A stars the maximum radiation intensity lies in the ultra-violet (0.3μ to 0.4μ) while in the cooler (Class K and M) stars the maximum emission lies at 0.7μ to 0.9μ in the infra-red.

A calculation is made of the spectral component radiations of a black body at various temperatures, using the spectral transmission data on these screens. From a comparison of the observed and the calculated spectral radiation components, it appears that the black body temperature (that is, the temperature which a black body would have to attain in order to emit a similar relative spectral energy distribution) varies from 3000° K. for red, Class M, through 6000° K. for the yellow, solar type stars to 10,000° K. or perhaps even higher for blue, Class B, stars.

The observing station being much higher (7300 feet as compared with 4000 feet) than previously used, the atmospheric scattering of light was greatly reduced, and consequently the transmissions of the violet are somewhat higher than previously observed when the water cell was interposed. However, all the data verify previous measurements showing that red stars emit three to four times as much infra-red radiation as blue stars of the same visual magnitude. Moreover, observations made on the same night (same weather conditions) are consistent in showing small gradations in the infra-red radiation components, corresponding with the small gradations (say B2 and B8) in spectral types.

For binary stars having companions of low luminosity the water-cell transmissions are low, indicating that the companion stars emit considerable infra-red radiation.

Among the subsidiary investigations made with a view to the improvement of stellar radiometers, this paper gives data on the radiation sensitivity of thermocouples of alloys of gold-palladium, platinum-rhodium, bismuth-tin, bismuth-antimony, and also of pure bismuth.

CARBON MONOXIDE IN PRODUCTS OF COMBUSTION FROM NATURAL GAS BURNERS.[8]

By I. V. Brumbaugh and G. W. Jones.

[ABSTRACT.]

CARBON MONOXIDE, a very poisonous gas, is produced in combustion processes where there is a deficiency of oxygen for completely burning the carbon in the gas to carbon dioxide. Conditions favorable for the production of carbon monoxide result with the usual type of gas burner when the flame is insufficiently aerated. It occurs if the burner is placed too close to the utensil.

Carbon monoxide combines with the hemoglobin of the blood and temporarily destroys its function as an oxygen carrier. The affinity of carbon monoxide for hemoglobin is 250 to 300 times as great as oxygen, and it is easily seen why a small percentage of carbon monoxide soon becomes very dangerous to health when inhaled for some time. The maximum percentage of carbon monoxide allowable for continuous exposure from a hygienic standpoint should not be greater than 0.02 per cent., and for intermittent exposures of 1 hour, not greater than 0.04 per cent.

It is known that the efficiency of natural gas burners can be greatly increased by placing the burner close to the utensil. It is, therefore, very important to know how close the burner can be placed to the utensil without producing dangerous quantities of carbon monoxide. In this connection it is necessary to make a study of the effect of different types of flames on the production

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[8] Technologic Papers No. 212.

of carbon monoxide. Different types of flames are obtained by changing the position of the air shutter so as to change the amount of primary air injected into the burner with the gas.

Tests for carbon monoxide were made with top burners of standard-size at rates of consumption of 6.0 and 8.0 cubic feet per hour (6480 and 8640 Btu per hour). From the many tests made under a variety of conditions the maximum quantity of carbon monoxide was found to be 0.25 cubic foot per hour. Taking for comparison a room of 1000 cubic feet capacity, which can be considered as representative of the size of the average kitchen, and taking 0.04 per cent. of the maximum limit of carbon monoxide permissible for healthful conditions for 1 hour's exposure, it would take over 1½ hours before the concentration reached 0.04 per cent. if only one burner was operated and the room was unventilated. If as many as four burners were used under the same condition at one time, the carbon monoxide would have increased to 0.04 per cent. in less than half an hour.

It was observed that no carbon monoxide was found where the distance of the utensil from the burner was such that the blue inner cone of the flame did not touch the utensil.

For the same rate of consumption and the same ratio of primary air to gas one design of burner may permit the utensil to be placed as close as ¾ inch, while another design may require a distance of more than 1¼ inches in order that the amount of carbon monoxide be negligible.

For a given air shutter setting which determines the ratio of primary air to gas, the highest percentages of carbon monoxide are produced when the utensil is placed so close to the burner as to cause a "floating flame." When using the same burner with the utensil at a position that causes the flame to float, the carbon monoxide increases as the primary air rate is decreased. Therefore, a yellow flame will produce carbon monoxide at a rate greater than a blue flame.

Much of the carbon monoxide is surely produced by the smothering of the flame with the products of combustion, which are hindered in their escape at the close positions of utensil from burner by the unavoidable baffling of the supply of secondary air. It is generally reported that carbon monoxide is produced by the chilling of the flame with a relatively cold surface.

Ventilation is essential where gas is consumed. Normal air contains 20.9 per cent. of oxygen. A natural gas flame was found to be smothered from deficiency of oxygen when the content of the atmosphere had been diminished to about 15.5 per cent. A very dangerous amount of carbon monoxide was found to be present at the condition where the flame was smothered out.

Under the worst conditions of top burner operation the amount of carbon monoxide liberated by the five different burners tested was not enough to be dangerous to health unless one worked directly over the burner or several burners were in use at the same time for several hours, or the room was unventilated.

When one considers the natural ventilation which takes place through the windows and doors it would seem that the danger from carbon monoxide poisoning with natural gas top burners is quite remote.

Leather and Humidity. (*U. S. Department of Agriculture, Press Service Sheet No. 205.*)—The strength and elasticity of leather are greater when the air is moist than when it is dry, and for this reason, says the Bureau of Chemistry, it is important in making comparative tests of leather to be sure that all pieces tested are under the same humidity conditions. A good piece of leather tested in a dry atmosphere might appear to be weaker than a much poorer piece tested when the air was moist.

Tests made of more than 500 pieces taken from the most uniform part of the hide, alternate strips being subjected to dry air and damp air at a temperature of 70° F., showed that an increase from 35 per cent. relative humidity to 55 per cent. increased the strength of the leather 13 per cent. and the stretch 16 per cent. When the humidity was raised from 35 per cent. to 75 per cent. the average increase in strength was 42 per cent. and in stretch 53 per cent.

It is apparent that control of the humidity in a room where leather is tested is necessary if the results are to be worth anything. The Bureau of Chemistry has devised such a room in which the amount of moisture in the air may be kept uniform and at any percentage of saturation continuously. It is the only testing room in the world where the conditions are controlled so well.

The United States spent $600,000,000 for roads in 1921, according to estimates of the Bureau of Public Roads, United States Department of Agriculture. This sum was derived from the following sources: Local road bonds, 33 per cent.; county, township, and district taxes, assessments, and appropriations, 14 per cent.; state taxes and appropriations, 12 per cent.; state road bonds, 7 per cent.; motor vehicle license revenues, 19 per cent.; Federal aid, 14 per cent.; and miscellaneous sources, 1 per cent.

On Atoms and Molecules. ALBERT C. CREHORE. (*Phil. Mag.*, May, 1922.)—It must not be supposed that the regnant Rutherford atom alone is being considered. In this article you will find a photograph of models of the lighter elements and of their isotopes, wherein there is a far departure from the arrangement of a positively charged nucleus with its satellites of electrons.

G. F. S.

On the Molecular Scattering of Light in Water and the Color of the Sea. C. V. RAMAN. (*Proc. Royal Soc.*, A 708.)—"The theory that the light of the sky owes its origin and colour to diffraction by the molecules of the atmosphere is now established on a firm experimental basis by the brilliant work of Cabannes and of Lord Rayleigh on the scattering of light by dust-free gases, and by the measurements of the transparency of the higher levels of the atmosphere in the visual region of the spectrum, which have yielded results in close agreement with the calculated values. It is the purpose of the present paper to point out the part played by molecular diffraction in another of the great natural optical phenomena, that is, the colour exhibited by large masses of clear water when illumined by sunshine and viewed from above, the depth being so great as to provide a perfectly black background for observation."

The "theory of fluctuations," developed by Einstein and Smoluchowski, is applied to the problem and a formula is obtained in which the outstanding relation is this. When a beam of light is traversing a body of water the intensity of the light diffused perpendicularly to the direction of the ray is inversely proportional to the fourth power of the wave-length of the light. "Volume for volume, water at 30° should scatter light 159 times as strongly as dust-free air under standard conditions." The result of the operation of the inverse fourth power law is that the shorter wave-lengths, the blue and violet, are diffused laterally to a much greater extent than the long reds and yellows.

The author combats Lord Rayleigh's view that the blue of the sea is due to reflected skylight. "Light reflected at the polarising angle from the surface of a liquid may be quenched by observation through a suitably oriented nicol. Hence by observing a tolerably smooth patch of water through a nicol at the polarising angle, the surface reflection may be got rid of. During a recent voyage, the writer made some observations by this method in the deeper waters of the Mediterranean and Red Seas, and found that the colour of the sea, so far from being extinguished when the sky-reflection is cut off is seen with wonderfully improved vividness and with saturated hues."

The entire trend of this paper is in opposition to the opinion that the color of large masses of water is due either to absorption or to reflection or to the presence of suspended matter. The scattering of the light is ascribed to the molecules of water.

G. F. S.

NOTES FROM THE RESEARCH LABORATORY EASTMAN KODAK COMPANY.*

NOTE ON PROFESSOR SVEDBERG'S METHOD OF GRAIN ANALYSIS OF PHOTOGRAPHIC EMULSIONS.[1]

By S. E. Sheppard and A. P. H. Trivelli.

[ABSTRACT.]

F. F. Renwick has suggested that the method of Svedberg may have left grains incompletely developed. On removing the developed grains and measuring, the partly removed grains would be measured as whole grains with smaller dimensions. The authors have investigated this by removing the developed grains with pure chromic acid which left a ghost of the grain composed of red silver chromate together with oxides of chromium. The photomicrograph then showed a sharp distinction between the developed and undeveloped grain. It was found in the case of two minutes' development with pyro that the grains develop completely so that Svedberg's method is a valuable and reliable method of optical analysis.

Burning of One Hundred Tons of Picric Acid.—Picric acid was packed in barrels, each containing approximately 400 pounds of the acid. An open shed magazine contained 500 barrels of the acid. Red hot carbon, forced from the exhaust of a tractor ignited, exposed picric acid which had sifted from the barrels. The entire 100 tons of picric acid were consumed in the resulting fire. The flames reached a height of 35 to 40 feet, and had a reddish color. The heat was so intense that the metal in the roof and in the barrel hoops was melted, and a portion of it was completely burned. Abundant heavy black smoke was noted during the early stage of the fire; however, combustion of the carbon became more complete as the temperature increased (Charles E. Monroe, *Jour. Ind. Eng. Chem.*, 1922, xiv, 552–554).

J. S. H.

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* Communicated by the Director.

[1] Communication No. 137 from the Research Laboratory, Eastman Kodak Company, and published in *Phot. J.*, (London) April, 1922, p. 196.

On Seeing Ultramicroscopic Particles with the Naked Eye. J. Traube and P. Klein. (*Physik. Z.*, April 15, 1922.)—When a beam of light passes through an optically empty liquid, its path there is invisible, though the places of entrance and of exit may be seen. In a colloidal solution, on the other hand, the path appears as a uniformly illuminated cloudy space. If any particle can be seen by itself, by the naked eye, within this space, it must be large enough to be seen in like manner elsewhere. The authors happened to notice that the addition of sodium carbonate to a solution of lead nitrate gave rise to a cloud space along the path of the light in which individual particles could be seen. The result was obtained upon adding two drops of a one-half normal sodium carbonate solution to 30 c.c. of a one-thirty thousandth normal solution of lead nitrate. When the path of light was observed with a lens there was seen for somewhat less than a minute a swarm of particles in violent but irregular motion. A minute later the unaided eye at a distance of five metres could see the same thing.

This effect is similar to the Brownian Movements. The particles concerned are of extremely small dimensions. In one instance where the effect was well seen no inhomogeneity of the liquid could be seen under a microscope of high magnification.

The effect can be obtained only with solutions of certain concentrations, though a number of different solutions may be used. Siedentopf of Jena explains it as a diffraction phenomenon connected with tiny needle-like crystals.

G. F. S.

Contamination of Air with Carbon Monoxide.—Yandell Henderson and Howard W. Haggard, of Yale University (*Jour. Ind. Eng. Chem.*, 1922, xiv, 229–236), draw the following conclusions from their experiments in which the period of exposure was several hours. The time of exposure in hours is multiplied by the concentration of the carbon monoxide in parts per 10,000 of air. If the product equal 3, no perceptible physiological effect is noted; if it equal 6, the effect is just perceptible; if it equal 9, headache and nausea are produced; if it equal or exceed 15, conditions are dangerous to life. Exercise and physical work increase the rate of absorption of carbon monoxide from a contaminated atmosphere. Upon return to fresh air, the carbon monoxide which has been absorbed by the blood, is excreted through the lungs; from 30 to 60 per cent. of the absorbed carbon monoxide is excreted hourly. Carbon monoxide is the only toxic constituent of importance in the exhaust gas from gasoline. Illuminating gas and the exhaust gas from coal tar distillate contain other toxic constituents as well as carbon monoxide. J. S. H.

NOTES FROM THE U. S. BUREAU OF CHEMISTRY.*

SOME CHANGES IN THE COMPOSITION OF CALIFORNIA AVOCADOS DURING GROWTH.[1]

By C. G. Church and E. M. Chace.

[ABSTRACT.]

If packed too early, the avocado has a tendency to shrivel and become "rubbery," is watery, and lacks the characteristic flavor of well-matured fruit. Thus its maturity problem is of special importance. The Bureau of Chemistry has recently completed an investigation on the composition of several varieties of the avocado at the various stages of its growth.

No satisfactory correlations between physical properties and maturity were found in the avocados examined.

The proportion of many of the constituents of the avocado changes during its development, the most marked change being the increase of the fat content. This takes place rapidly while the fruit is immature, and much more slowly as it approaches maturity, with possibly a slight decrease if the fruit remains too long upon the tree. It is accompanied by a decrease in sugar content.

Fruits rich in fat (above 20 per cent.) contain at least 70 per cent. of that constituent on a water-free basis at maturity.

On storage of immature fruits there is an apparent increase in the proportion of fat, accompanied by a decrease in the sugar content and undetermined matter.

Mature fruits on storage do not show this increase to the same extent, and at times show some loss.

No standards of maturity are recommended.

A COLOR TEST FOR "REMADE MILK AND CREAM."[2]

By O. L. Evenson.

[ABSTRACT.]

A practical qualitative test for distinguishing natural pasteurized milk from a mixture of natural and remade milk has

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* Communicated by the Chief of the Bureau.

[1] Issued as *U. S. Dept. Agr. Bul. 1073,* May, 1922.

[2] Published in *J. Dairy Sci.,* 5 (1922): 97.

been devised. This test is based upon the discovery that a yellow color is produced when the worked curd of milk made from milk powder is treated with sodium hydroxid. The color is probably due to the combination of a trace of lactose with the protein during the process of manufacturing the milk powder.

THE PROTEINS OF THE TOMATO SEED, SOLANUM ESCULENTUM.[3]

By C. O. Johns and C. E. F. Gersdorff.

[ABSTRACT.]

ANALYSES of five samples of tomato seed and press-cake show an average content of 36.91 per cent. of protein ($N \times 6.25$). The total globulins were extracted from the press-cake by extraction with 0.5 per cent. sodium hydroxid. Preparations obtained from these extractions gave uniform results on analysis. From seed of high germinating quality two globulins, α and β, have been isolated and analyzed. These globulins, coagulable by heating for ten minutes at 74 and 96° C., are precipitated from their saline solutions by 0.3 of saturation, in the case of the α-globulin, and by saturation with ammonium sulphate, in the case of the β-globulin. They differ in their solubility, the α-globulin being easily denatured, while the β-compound is highly soluble in mere traces of aqueous sodium chloride.

The elementary analyses of the two globulins show the following percentage of differences in composition: The α-globulin contained carbon, 52.29, nitrogen, 18.34, and sulphur, 1.16; while the β-globulin contained carbon, 51.21, nitrogen, 16.02, and sulphur, 0.81. The sulphur content of the globulins is in the ratio of 3 : 2. The analyses by the Van Slyke method show that the nutritionally essential basic amino acids are well represented in these globulins.

It is of interest to note that these globulins are high in both arginine and lysine. The β-globulin contains also an unusually large proportion of histidine, while in the α-globulin the histidine content is low. Both globulins respond to the qualitative tests for tryptophane and tyrosine. In the distribution of the nitrogen based on the weight of the proteins, as calculated from the Van

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[3] Published in *J. Biol. Chem.*, **51** (1922): 439.

Slyke analyses, the most marked difference is found in the figures for the non-basic nitrogen.

Tests failed to disclose the presence of albumin and glutelin.

A CHEMICAL STUDY OF THE PROTEINS OF THE ADSUKI BEAN, PHASEOLUS ANGULARIS.[4]

By D. B. Jones, A. J. Finks, and C. E. F. Gersdorff.

[ABSTRACT.]

THE adsuki bean contains about 21.13 per cent. of protein ($N \times 6.25$), 16.7 per cent. of which is extracted by means of a 5 per cent. aqueous sodium chloride solution.

By fractional precipitation of the sodium chloride extracts with ammonium sulphate two globulins, designated as the α- and β-globulins, have been isolated. The former was precipitated by the addition of ammonium sulphate in sufficient amount to make the original extract 0.3 saturated. A small fraction consisting of a mixture of the two globulins was separated from the filtrate by increasing the concentration of ammonium sulphate up to 0.65 of saturation. This fraction was discarded, and the β-globulin was precipitated by making the solution completely saturated. A small quantity of an albumin was found in distilled water extracts of the bean, after the globulins had been removed.

The two globulins differ markedly in their sulphur and nitrogen content and in their nitrogen distribution, as determined by the method of Van Slyke.

Proper Use of Coal.—Bulletin No. 9, just issued by the Department of Internal Affairs of Pennsylvania, contains a paper by G. H. Ashley, State Geologist, advocating strongly a more economical use of coal, especially the coking-coals of the State.

The high volatile coals of Pennsylvania can be made to yield from four to six times the quantity of oil now being obtained from the State wells. In view of this, we are surely not justified in burning raw soft coal for raising steam when the yield of hydrocarbons is thus diminished. One authority, perhaps a little enthusiastic, has declared that within a few years it will be against the law to burn such coal. This is a desirable result, but it may not be very near at hand. Pennsylvania coking-coals were used for over eighty years in beehive ovens, but all the gaseous products were lost. It is not merely the tar and volatile hydrocarbons that are thus destroyed;

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[4] Published in *J. Biol. Chem.*, **51** (1922): 103.

a considerable amount of ammonia is wasted. The value of ammonia in modern industries is now recognized, especially when we recall the vast amount of money and scientific investigation which Germany lavished on the synthetic ammonia process. Our ordinary methods of steam-making are wasteful of fuel as such, apart from the attendant objection from smoke. Greater efficiency has been obtained of late years, but even with the best conditions the results are not comparable to those obtained with liquid fuels in internal combustion engines.

The increasing use of gasolin and the rapid depletion of the oil reserves of the United States and Mexico will compel searches for other sources of liquid fuel. Two such sources are now attracting much attention, the oil-shales and coal. Exploitation of the former is still in the experimental stage, but the distillation of coal is, in the main, a solved problem. By-product coke ovens are often operated at a rather high temperature. A slightly larger yield of coke can be obtained from the by-product oven than from the beehive form. Coke is a smokeless fuel, very much of the type of anthracite, but not nearly so compact and, therefore, burning more rapidly. The use of coke in domestic heating in the winter would be satisfactory along all lines except that a greater storage capacity would be needed and visits to the furnace would be somewhat more frequent. The proportion of light and heavy oil and of gas obtained from a given coal can be modified by the temperature, and experiments on the low temperature distillation are reaching the stage of commercial production in England, Germany and the United States. One ton of Kentucky coal containing 3 per cent. of moisture, 35 per cent. volatile matter, 55 per cent. fixed carbon and 7 per cent. ash, is said to yield 1400 pounds of carbocoal, 30 gallons of tar, 9000 cubic feet of gas, 20 pounds of ammonium sulphate, and 2 gallons of light oil thrown down from the gas.

The term "carbocoal" refers to a product obtained in Virginia by a special process of distillation. It is softer than ordinary coke and contains from 8 to 10 per cent. of volatile matter. It could be used at the point of production, but is said to be not suited to the general market. It is, however, employed in the manufacture of briquets, which are stated to be of good quality.

The tar contains no naphthalene but is rich in tar-acids and cresols, and contains more phenol than in other forms of tar. So far as Pennsylvania coal is concerned, it has been estimated from the results obtained in England, that by carbonizing the 140,000,000 tons of bituminous coal now mined in Pennsylvania, in a year, more than 400,000,000 gallons of motor fuel and one billion and a quarter gallons of Diesel and lubricating oils could be obtained. The total of these figures is about five times the quantity of oil now being produced in Pennsylvania. In addition over a million tons of ammonium sulphate would be obtained and the fixed residue, amounting to over a hundred million tons, would be an excellent smokeless fuel. H. L.

NOTES FROM THE U. S. BUREAU OF MINES.*

SEPARATION OF PALLADIUM AND PLATINUM.

By C. W. Davis.

In the investigation of methods for assaying platinum conducted by the Bureau of Mines, recent experiments have developed that with certain ores, especially when the quantity of platinum is considerable, nitric acid will not effect a separation of platinum and palladium.

Wunder and Thuringer[1] have developed methods for the separation of palladium from all the platinum metals except platinum by means of dimethylglyoxime. All of their precipitations were carried out while the solutions were being heated. This caused a partial precipitation of the platinum along with the palladium.

A few preliminary tests substantiated the belief that palladium could be precipitated free from platinum if a solution of the chlorides of these metals be treated at room temperature with an alcoholic solution of dimethylglyoxime. The following procedure was worked out to separate and determine platinum and palladium quantitatively.

The platinum and palladium free from the other platinum metals are obtained by the method given in U. S. Bureau of Mines Technical Paper 270. These metals are ignited and cooled in an atmosphere of hydrogen and weighed together. The weighed metals are dissolved in a little aqua regia and evaporated just to dryness. The residue is moistened with a drop of hydrochloric acid and after the addition of a little distilled water, a solution of dimethylglyoxime is added, drop by drop, with constant stirring until there is no further precipitation. After standing at room temperature for a few minutes the voluminous yellow precipitate is filtered off, washed thoroughly with distilled water and ignited slowly and carefully, first in air to drive off organic matter and then in hydrogen to reduce any oxidized palladium to the metal. The metallic palladium is then weighed.

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* Communicated by the Director.

[1] *Comp. rend,* t. 30, 1913, p. 12.

The platinum may be found by difference or it may be recovered and weighed. To recover the platinum the filtrates from the palladium precipitation are carefully evaporated to dryness in a small pyrex beaker or porcelain dish, a little nitric acid being added as the volume becomes small. The residue is heated almost to redness to drive off all organic matter, the presence of which would prevent the complete precipitation of platinum. The residue is extracted with a little aqua regia, is evaporated just to dryness, is extracted with a drop of hydrochloric acid, and is diluted with a little distilled water. The solution is made alkaline with sodium carbonate, acidified with an excess of formic acid, and boiled to precipitate the platinum, which is filtered off, washed, ignited, and weighed. Further details are given in a recent publication of the Bureau.

THE SULPHUR DIOXIDE LEACHING PROCESS.

By Charles E. van Barneveld.

The sulphur dioxide leaching process, developed at the Southwest experiment station of the U. S. Bureau of Mines, Tucson, Arizona, was devised to provide a cheap and efficient method for treating the so-called "porphyry" copper ores of the Southwest which generally contain both "sulphide" and "non-sulphide" copper minerals, mixed in such proportions that they can only be satisfactorily treated by a method which will concurrently recover both the sulphide copper and the non-sulphide copper. The latter term has been adopted to include all the minerals commonly referred to in operating phraseology in the mills of the Southwest as "oxidized," "oxide," or "soluble" copper. The process was developed with the coöperation of the Miami Copper Company and the Arizona Copper Company, and is suitable and commercially available for a wide range of ores.

While the process is called an SO_2 leaching process, it is in no sense an offshoot or development of the early Neill-Burfeind "leaching" process or of later modifications thereof which involve the retention of all dissolved copper in solution as copper sulphite, a notoriously unstable compound, to be later precipitated as cupro-cupric sulphite (Cu_2SO_3, $CuSO_3$). Instead, it is a continuous leaching process controlled to form solutions of copper sulphate direct from oxidized copper ore, ranging in fineness from 20 to 48 mesh, pulped with water containing the usual proportion of reclaimed mill liquid, treated counter-current with dilute SO_2 roaster gas containing a large excess of oxygen over the amount necessary to completely oxidize all sulphites formed. Thus all difficulties met with in the aforementioned processes from the formation of unstable complex copper salts are avoided. No attempt is made to regenerate the leaching solutions; the sulphur supplied finally goes to waste as sulphates of the acid-soluble constituents of the ore, and as iron sulphates formed during precipitation of dissolved copper on iron.

Sulphur dioxide made from any convenient source, such as native sulphur, massive pyrite, or concentrate carrying upwards of 20 per cent. sulphur, may be utilized. If smelter gases containing 2 per cent. SO_2 by volume are available, they may be utilized direct from the stack. The ordinary volatile impurities found in smelter gases, such as arsenic and antimony, are not detrimental in this application of SO_2 leaching. Further details are given in a report issued by the Bureau in mimeograph and in more complete form in Technical Paper 312, now in course of publication.

ACETYLENE NOT A PRECIPITANT FOR CYANIDE SOLUTIONS.

By John Gross.

IN connection with some investigations being made by the Bureau of Mines, on the precipitation of gold and silver from cyanide solutions, it was suggested that the effect of acetylene for this purpose be investigated.

The acetylene used in the tests was from commercial calcium carbide. Experiments resulted in more or less complete precipitation of silver, but no gold.

As silver acetylene, obtained by precipitating the silver from an ammoniacal solution of silver nitrate by acetylene, is yellowish white, easily soluble in cyanide and highly explosive, and the precipitate obtained from the cyanide solutions was black, not soluble in cyanide and not explosive, it was decided to investigate the nature of the silver precipitate from the cyanide solutions. In preparing a large quantity of the precipitate it was found that after complete precipitation of the silver the solution contained soluble sulphides. This provided a clew and after appropriate tests the precipitation was proved to be silver sulphide.

The conclusion drawn was that a small amount of hydrogen sulphide was contained in the acetylene and that this was the active precipitating agent. Other tests were made, all of which verified the conclusion that acetylene, free from hydrogen sulphide, had no precipitating power on cyanide solutions of silver or gold. Further details are given in a recent report issued by the Bureau.

A Photographic Spectrum of the Aurora of May 13-15, 1921, and Laboratory Studies in Connection with It. Lord Rayleigh. (*Proc. Royal Soc.*, A 709.)—A very good photograph of the spectrum was obtained on the night of May 14. On the plate there appears a trace of a continuous spectrum, to be attributed to moonlight, the negative nitrogen bands in the blue, the violet and the ultra-violet and yellow-green aurora line. Strangely enough the bands are stronger than the line. When the spectrum of krypton was photographed on the same plate its characteristic line appeared in "approximate coincidence" with the auroral line.

It was not found possible to reproduce in the laboratory the nitrogen bands as they manifested themselves in the light of the aurora. Through excitation of nitrogen by atomic rays a good imitation was got, but other spectra of the gas persisted in appearing under the conditions of experiment. The cathode ray spectrum in nitrogen was free from these spectral interlopers but the distribution of intensity among the bands was not the same as in the aurora.

"We have reason to believe, not indeed from direct experiment, but on very strong theoretical grounds, that the upper atmosphere, in which the aurora occurs, is rich in the lightest constituents of air, helium and (possibly) hydrogen. Do these constituents appear in the auroral spectrum? The photographs reproduced confirm clearly all previous evidence that they do not. We are faced, therefore, with the alternatives that either they are not there, or that the conditions of excitation are not such as to develop the spectrum. According to all laboratory experience, even a trace of hydrogen asserts itself in the spectrum of any kind of an electric discharge through air, under any conditions of pressure." The origin of the aurora is not definitely known. "There is a good deal of evidence from the work of Birkeland, Stormer, and Vegard, for attributing the aurora to cathode rays from the sun." An objection to this explanation is that, as stated above, in the laboratory cathode rays fail to give the desired distribution of intensity in the band spectrum of nitrogen. On other grounds the author finds it very difficult to account for the origin of the aurora on the basis of excitation by atomic rays, even though these in the laboratory do give the same intensity distribution as that in the auroral spectrum. G. F. S.

THE FRANKLIN INSTITUTE.

COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of Stated Meeting held Wednesday, June 7, 1922.)

Hall of the Institute,
Philadelphia, June 7, 1922.

Dr. James Barnes *in the Chair.*

The following report was presented for final action:

No. 2784: Vaphor Phase Oxidation of Benzene to Maleic Acid. The Howard N. Potts Medal Jointly to Messrs. John Morris Weiss and Charles R. Downs, of New York.

The following reports were presented for first reading:

No. 2767: Audion.
No. 2790: Automatic Cashier.

R. B. Owens,
Secretary.

MEMBERSHIP NOTES.

ELECTION TO MEMBERSHIP.

(Stated Meeting, Board of Managers, June 14, 1922.)

RESIDENT MEMBERSHIP.

Mr. Murray C. Boyer, Solicitor of Patents, 806 Franklin Trust Building, Philadelphia, Pennsylvania.

NON-RESIDENT MEMBERSHIP.

Mr. James A. Wright, Wright-Fisher Engineering Company, Detroit, Michigan.

CHANGES OF ADDRESS.

Mr. George E. Cabot, 60 State Street, Boston, Massachusetts.
Mr. James H. Dawes, 1310 Arch Street, Philadelphia, Pennsylvania.
Mr. Patrick B. Delany, Nantucket, Massachusetts.
Mr. J. H. Gravell, 1126 S. Eleventh Street, Philadelphia, Pennsylvania.
Mr. W. O. Griffith, The Clearing, Saunderstown, Rhode Island.
Mr. G. S. Lawler, Associated Factory Mutual Fire Insurance Companies, Fort Hill Square, 184 High Street, Boston 9, Massachusetts.

MR. F. MACMURPHY, Wheaton, Minnesota.
PROF. I. M. RAPP, Phœnixville, Pennsylvania.
MR. G. BERKELEY REED, Rowayton, Connecticut.
MR. N. W. SMITH, Broad Street Station, Philadelphia, Pennsylvania.
MR. S. D. SPRONG, Atlantic Utilities Corporation, 2 Rector Street, New York City, New York.

NECROLOGY.

Mr. Charles A. Lindstrom, Pressed Steel Car Company, Pittsburgh, Pennsylvania.

Dr. Walter L. Pyle, 1931 Chestnut Street, Philadelphia, Pennsylvania.

LIBRARY NOTES.

PURCHASES.

DEERR, NOEL.—Cane Sugar. 1921.
FLEMING, J. A.—Fifty Years of Electricity. 1921.
FRANÇOIS, L.—Les Aliments Sucrés Industriels. n.d.
GEERLINGS, H. C. P.—Chemical Control in Cane Sugar Factories. 1917.
GEERLINGS, H. C. P.—Practical White Sugar Manufacture. 1915.
GEERLINGS, H. C. P.—The World's Cane Sugar Industry Past and Present. 1912.
GIRARD, A. L.—Les sucrés, le café, le thé, le chocolat. 1907.
GROBERT, J. DE, and Others.—Traité de la Fabrication du Sucré, 2 vols. 1913.
HERIOT, H. T. P.—Science in Sugar Production. 1907.
JONES, L., and F. I. SCARD.—The Manufacture of Cane Sugar. 1921.
MAXWELL, FRANCIS.—Sulphitation in White Sugar Manufacture. 1916.
PETRIE, TELFORD.—Modern Practice in Heat Engines. 1922.
ROUX, E., and C. F. MUTTELET.—Aliments Sucrés. 1914.
SAILLARD, ÉMILE.—Betterave et Sucrerie de Betteraves. 1913.
SIDERSKY, D.—Manuel de Chimiste de Sucrerie. 1909.
STEWART, ALFRED W.—Some Physico-chemical Themes. 1922.
TEYSSIER, R.—La Sucrerie. n.d.
THORPE, SIR E.—Dictionary of Applied Chemistry, Vol. 3. 1922.

GIFTS.

L'Academie Royale de Belgique, "L'Academie Royale de Belgique depuis sa Fondation (1772-1922)." Brussels, Belgium, 1922. (From the Academy.)
Acme Wire Company, Acme Wire Products. New Haven, Connecticut, 1922. (From the Company.)
Adams Company, Bulletins 104, 105, 106, 125 and 152 of Squeezers and Molding Machines. Dubuque, Iowa, no date. (From the Company.)
Alberger Heater Company, Heating and Cooling Equipment. Buffalo, New York, 1921. (From the Company.)
Alemite Die-Casting and Manufacturing Company, Catalogue No. 5. Chicago, Illinois, 1922. (From the Company.)

American Blower Company, General Catalogue "A B C" Products. Detroit, Michigan, 1922. (From the Company.)

American Car and Foundry Company, Berwick Electric Metal Heaters. New York City, New York, 1922. (From the Company.)

American Engineering Company, Windlasses, Steering Gear and Capstans Catalogues. Philadelphia, Pennsylvania, 1922. (From the Company.)

American Institute of Chemical Engineers, Report of Committee on Chemical Engineering Education. Brooklyn, New York, 1922. (From the Institute.)

American Manganese Bronze Company, Bronze Products of Quality for Engineering Purposes. Holmesburg, Philadelphia, Pennsylvania, 1922. (From the Company.)

Anderson, H. P., and Company, Modern Methods for Maintaining Roads and Streets. Chicago, Illinois, no date. (From the Company.)

Atchison, Topeka and Santa Fe Railway Company, Twenty-seventh Annual Report for year ending December 31, 1921. New York City, New York, 1921. (From the Secretary.)

Austin Machinery Corporation, Trenching Machines and Backfilling Machines. Chicago, Illinois, 1922. (From the Corporation.)

Barduff, Limited, Barduff Book of Motoring Wrinkles and Recipes. London, England, 1922. (From the Company.)

Bates Machine Company, Cookson Feed Water Heaters and Receivers. Joliet, Illinois, 1922. (From the Company.)

Beaumont, R. H., Company, Catalogues 34 and 45 and Book 36 on Ashes. Philadelphia, Pennsylvania, no date. (From the Company.)

Bethlehem Steel Company, Catalogue of Bolts, Nuts and Rivets. Bethlehem, Pennsylvania, 1920. (From the Company.)

Bradford Machine Tool Company, Catalogue No. 25 of Bradford Lathes. Cincinnati, Ohio, 1922. (From the Company.)

British Columbia Department of Mines, Report of the Minister of Mines for 1921. Victoria, British Columbia, 1922. (From the Minister.)

Broadbent, Thomas, and Sons, Limited, Automatic Centrifugal Clutches. Huddersfield, England, 1922. (From the Company.)

Brown Hoisting Machinery Company, Booklet 4-22. Cleveland, Ohio, 1922. (From the Company.)

Bucyrus Company, Bulletin C-142 of Revolving Shovels. South Milwaukee, Wisconsin, no date. (From the Company.)

Budd Grate Company, Budd Combustion Arch System and Smokeless Combustion. Philadelphia, Pennsylvania, 1922. (From the Company.)

Buffalo Forge Company, Catalogue of Bulletins 300 to 319. Buffalo, New York, no date. (From the Company.)

Buffalo, Rochester and Pittsburgh Railway Company, Thirty-seventh Annual Report for the year ending December 31, 1921. New York City, New York, 1921. (From the Secretary.)

Burhorn, Edwin, Company, Cooling Towers. New York City, New York, 1922. (From the Company.)

Caldwell, W. E., Company, Friction Clutch Catalogue No. 1. Louisville, Kentucky, no date. (From the Company.)

Canada Dominion Bureau of Statistics, Railway Statistics for the year ended December 31, 1920. Ottawa, Canada, 1921. (From the Bureau.)

Cement Gun Construction Company, Book of Views showing Recent Work by Company. Chicago, Illinois, 1922. (From the Company.)

Chicago Fuse Manufacturing Company, Electrical Protecting Materials and Conduit Fittings. Chicago, Illinois, 1921. (From the Company.)

Churchill, Charles, and Company, Limited, Norton Grinding Wheels. London, England, 1922. (From the Company.)

Cincinnati Milling Machine Company, Cincinnati Cutter Grinders. Cincinnati, Ohio, 1919. (From the Company.)

Clarage Fan Company, Catalogue 6 of Vertical Steam Engines. Kalamazoo, Michigan, 1922. (From the Company.)

Clarkson College of Technology, Quarterly Bulletin, April, 1921. Potsdam, New York, 1921. (From the College.)

Columbia University, 33 Dissertations published in 1919, 1920 and 1921. New York City, New York. (From the University.)

Combustion Engineering Corporation, Lopulco Pulverized Fuel System for Locomotives. New York City, New York, no date. (From the Corporation.)

Concord Board of Water Commissioners, Fiftieth Annual Report for 1921. Concord, New Hampshire, 1922. (From the Commissioners.)

Consolidated Expanded Metal Companies, Hand-book of Design, Cop-al Metal Lath, Steelcrete Slab Tables, Steelcrete Products, Expanded Metal *versus* Bars. Braddock, Pennsylvania, 1922. (From the Companies.)

Cornell University, President's Report 1920-21. Ithaca, New York, 1921. (From the University.)

Dart, E. M., Manufacturing Company, Dart Union Fittings. Providence, Rhode Island, 1922. (From the Company.)

Domestic Engine and Pump Company, Bulletin Catalogue of Engines and Pumps. Shippensburg, Pennsylvania, 1922. (From the Company.)

Dow Chemical Company, How to Maintain Roads. Midland, Michigan, 1922. (From the Company.)

East Jersey Pipe Company, Hand Book of Pipe. New York City, New York, 1920. (From the Company.)

Edmundsons Electricity Corporation, Limited, Water Power and the Generation of Electricity. London, England, 1922. (From the Corporation.)

Electro Metallurgical Sales Corporation, Electromet Brand Ferro-alloys and Metals. New York City, New York, 1922. (From the Corporation.)

Elliott Company, Bulletin A, Strainers. Pittsburgh, Pennsylvania, 1922. (From the Company.)

Engineer Company, Oil Burning under Steam Boilers. New York City, New York, 1922. (From the Company.)

Erie Steel Construction Company, All-Steel Aggremeter. Erie, Pennsylvania, 1922. (From the Company.)

Excelsior Needle Company, Dayton Swagging Machine. Torrington, Connecticut, 1922. (From the Company.)

Ferry Cap and Set Screw Company, Catalogue No. 21, Ferry Process Screws. Cleveland, Ohio, 1922. (From the Company.)

Flannery Bolt Company, The Tate Flexible and F. B. C. Staybolt. Pittsburgh, Pennsylvania, 1922. (From the Company.)

Florida Railroad Commission, Twenty-fifth Annual Report, for the year ending February 28, 1922. Tallahassee, Florida, 1922. (From the Commission.)

General Chemical Company, Hard-n-Tyte Highways. New York City, New York, 1922. (From the Company.)

General Filtration Company, Incorporated, The Activated Sludge Process of Sewage Treatment. Rochester, New York, 1922. (From the Company.)

Grand Trunk Railway Company of Canada, Annual Report for the Year Ended December 31, 1921. Montreal, Canada, 1922. (From the Company.)

Grinnell Company, Five Factors in Heating Costs. New York City, New York, 1921. (From the Company.)

Harvard College, Seventy-sixth Annual Report of Astronomical Observatory, Observations and Investigations made at the Blue Hill Meteorological Observatory and Henry Draper Catalogue. Cambridge, Massachusetts, 1922. (From the College.)

Hazard Manufacturing Company, Hazard Keystone Wire. Wilkesbarre, Pennsylvania, 1922. (From the Company.)

Henderson, John M., and Company, Catalogue 54-2E. Aberdeen, Scotland, no date. (From the Company.)

Hendey Machine Company, The Hendey Machine Company 1870 to 1920. Torrington, Connecticut, 1922. (From the Company.)

Henry and Wright Manufacturing Company, Drilling Machines and Pamphlets B, C, H, HW, K, L. Hartford, Connecticut, no date. (From the Company.)

Illinois Stoker Company, Chain Grate Stokers, Catalogue L. Alton, Illinois, 1921. (From the Company.)

International Molding Machine Company, International Molding Machines, Catalogue 17. Chicago, Illinois, 1917. (From the Company.)

Koehring Company, Built to Endure. Milwaukee, Wisconsin, 1922. (From the Company.)

Lidgerwood Manufacturing Company, Bulletins 15 and 19. Philadelphia, Pennsylvania, 1922. (From the Company.)

Louisiana State Museum, Biennial Report of the Board of Curators for 1920-1921. New Orleans, Louisiana, 1922. (From the Museum.)

Ludlow Valve Manufacturing Company, Ludlow Valves and Fire Hydrants, 1921. Troy, New York, 1921. (From the Company.)

McClave-Brooks Company, Boiler Room and the Bank Balance. Scranton, Pennsylvania, 1922. (From the Company.)

McClintic-Marshall Company, Steel Construction. Pittsburgh, Pennsylvania, 1922. (From the Company.)

Machinery Forging Company, Flat Die and Upset Forgings. Cleveland, Ohio, no date. (From the Company.)

Meaker Galvanizing Company, Meaker Galvanizing Process. Chicago, Illinois, 1922. (From the Company.)

Metal Airscrew Company, Limited, Metal Propellers. London, England, 1922. (From the Company.)

Metal Forms Corporation, Metaform Interlocking Steel Forms for Circular Concrete Work. Milwaukee, Wisconsin, 1922. (From the Corporation.)

Milwaukee Locomotive Manufacturing Company, Milwaukee Gasolene Locomotives. Milwaukee, Wisconsin, 1922. (From the Company.)

Mine and Smelter Supply Company, Heusser Balances. New York City, New York. 1922. (From the Company.)

Minneapolis, St. Paul and Sault Ste. Marie Railway Company, Thirty-third Annual Report for year ended December 31, 1921. Minneapolis, Minnesota, 1922. (From the Company.)

Moloney Electric Company, Catalogue No. 215, Transformers. St. Louis, Missouri, 1922. (From the Company.) .

Murray Engineering Company, Power Plant Specialties. Chicago, Illinois, 1922. (From the Company.)

Murray Iron Works Company, Catalogue No. 85. Burlington, Iowa, 1919. (From the Company.)

Nashua Machine Company, New Bundy Steam Traps. Nashua, New Hampshire, 1922. (From the Company.)

National Lime Association, Lime Brief No. 251. Washington, District of Columbia, 1922. (From the Association.)

National Malleable Castings Company, Circulars 51, 52, 53, 54, 60, 61, 63, 65, 66, 67, 70 and Catalogues 2 and 22. Cleveland, Ohio, no date. (From the Company.)

National Pipe Bending Company, Bulletin No. 54. Philadelphia, Pennsylvania, 1919. (From the Company.)

National X-ray Reflector Company, X-ray Fixtures for Indirect Lighting and How to Know and Have Good Lighting. Chicago, Illinois, 1922. (From the Company.)

New Bedford Board of Health, Annual Report for 1921. New Bedford, Massachusetts, 1921. (From the Board.)

New York Blower Company, Catalogue No. 80. Chicago, Illinois, 1922. (From the Company.)

New York Edison Company, Electric Automobile Charging Stations in New York City and Vicinity. New York City, New York, 1922. (From the Company.)

New York Engineering Company, Ludlum Water Tube Marine Boiler. New York City, New York, 1922. (From the Company.)

Northern Equipment Company, Saving Fuel Automatically and Scientifically in the Boiler Room. Erie, Pennsylvania, 1920. (From DeVed-Kissick Company, Philadelphia, Pennsylvania.)

Nova Scotia Department of Public Works, Report on the Mines. Halifax, Nova Scotia, 1921. (From the Department.)

Ohio Body and Blower Company, Swartwout Metal Buildings. Cleveland, Ohio, 1922. (From the Company.)

O-K Clutch and Machinery Company, O-K Hoisting Machinery. Columbia, Pennsylvania, 1922. (From the Company.)

Oliver Machinery Company, Bulletins 1, 4 and 5. Grand Rapids, Michigan, no date. (From the Company.)

Ontario Department of Agriculture, Twenty-first Annual Report. Toronto, Canada, 1921. (From the Department.)

Ontario Department of Mines, Thirtieth Annual Report. Toronto, Canada, 1922. (From the Department.)

Page Steel and Wire Company, Page-Armco Welding Rods and Electrodes. Bridgeport, Connecticut, 1922. (From the Company.)

Parks Ball Bearing Machine Company, Catalogue C of Wood Working Machines. Cincinnati, Ohio, 1922. (From the Company.)

Partrick and Wilkins Company, Annunciators and Electrical House Goods. Philadelphia, Pennsylvania. 1922. (From the Company.)

Pawling and Harnischfeger Company, Bulletin 214, Drilling and Boring Machines. Milwaukee, Wisconsin, no date. (From the Company.)

Pennsylvania General Assembly, Appropriation Acts, Session of 1921. Harrisburg, Pennsylvania, 1921. (From the State Librarian.)

Philadelphia Bureau of Municipal Research, The Water Supply Problem of Philadelphia. Philadelphia, Pennsylvania, 1922. (From the Bureau.)

Philadelphia Rapid Transit Company, Rapid Transit Handbook. Philadelphia, Pennsylvania, 1922. (From Mr. Thomas E. Mitten.)

Pittsburgh-Des Moines Steel Company, Steel Water Tanks, Railway Service Tanks and Pittsburgh-Des Moines Steel Tanks. Pittsburgh, Pennsylvania, no date. (From the Company.)

Polytechnic Institute of Brooklyn, Catalogue of the College of Engineering 1922-1923. Brooklyn, New York, 1922. (From the Institute.)

Porter, H. K., Company, Porter Fireless Steam Locomotives and Porter Steam Locomotives. Pittsburgh, Pennsylvania, 1922. (From the Company.)

Pyle-National Company, Electric Lighting Equipment and Accessories for Locomotives. Chicago, Illinois, 1922. (From the Company.)

Railway Fire Protection Association, Proceedings of Eighth Annual Meeting, October, 1921. Chicago, Illinois, 1921. (From the Association.)

Richards-Wilcox Manufacturing Company, Conveying Equipment. Aurora, Illinois, 1922. (From the Company.)

Riter-Conley Company, Steel Plate Construction. Pittsburgh, Pennsylvania, 1922. (From the Company.)

Rockwood Manufacturing Company, Friction Transmission. Indianapolis, Indiana, 1920. (From the Company.)

Roth Brothers and Company, Bulletins 132, 133, 212, 215, 301 and 570. Chicago, Illinois, 1922. (From the Company.)

Russell Grader Manufacturing Company, Road Building and Earth Handling Machinery. Minneapolis, Minnesota, 1922. (From the Company.)

Schwarze Electric Company, Catalogue 9. Adrian, Michigan, 1922. (From the Company.)

Smith Engineering Works, Telsmith Crushers, Mounted Breakers, and Mining, Quarry and Gravel Pit Machinery. Milwaukee, Wisconsin, 1922. (From the Works.)

Southern Pine Association, The Use of Southern Yellow Pine in Car Construction. New Orleans, Louisiana, 1922. (From the Association.)

Sprague Electric Works, Sprague System Electric Motor Drive and Control for Newspaper Presses. New York City, New York, 1922. (From the Works.)

Springfield Machine Tool Company, Illustrated Catalogue J. Springfield, Ohio, 1919. (From the Company.)

Springfield Water Commissioners, Forty-eighth Annual Report for the year 1921. Springfield, Massachusetts, 1922. (From the Commissioners.)

Sterling Blower Company, Sterling Blowers and Blower Systems. Hartford, Connecticut, 1922. (From the Company.)

Sturtevant, B. F., Company, Bulletin No. 288. Boston, Massachusetts, 1921. (From the Company.)

Sunbury Manufacturing Company, The Sunbury Unloader. Sunbury, Ohio, no date. (From the Company.)

Terry Steam Turbine Company, The Terry Turbine. Hartford, Connecticut, 1922. (From the Company.)

Thew Shovel Company, Bulletins 111, 201, 501 and 601. Lorain, Ohio, 1922. (From the Company.)

Turbine Sewer Machine Company, Sewer Cleaning Equipment. Milwaukee, Wisconsin, 1922. (From the Company.)

Union Iron Works, Horizontal Return-tubular Boilers and Water Tube Boilers. Erie, Pennsylvania, 1922. (From the Works.)

United States Bureau of Census, United States Life Tables 1890, 1901, 1910 and 1901-10. Washington, District of Columbia, 1921. (From the Bureau.)

United Engineering Society, Engineering Foundation Report for the Year Ended February 9, 1922. New York City, New York, 1922. (From the Society.)

University of Delaware, Annual Catalogue 1921–1922. Newark, Delaware, 1921. (From the University.)

University of Florida, Catalogue 1921-1922. Gainesville, Florida, 1922. (From the University.)

University of North Dakota, General Catalogue 1921-1922. Grand Forks, North Dakota, 1922. (From the University.)

University of Virginia, Virginia Geological Survey Bulletin No. xxii. Charlottesville, Virginia, 1922. (From the University.)

Vibration Specialty Company, Eliminating Vibrations. Philadelphia, Pennsylvania, 1922. (From the Company.)

Wetmore Reamer Company, Wetmore Reamers. Milwaukee, Wisconsin, 1922. (From the Company.)

Whidden, Guy C., and Wilfred H. Schoff, Pennsylvanien und Seine Mannigfachen Betriebe. Philadelphia, Pennsylvania, 1912. (From Rev. Roland Ringwalt.)

Wilson-Maeulen Company, Fourteenth Pyrometer Catalogue. New York City, New York, 1922. (From the Company.)

BOOK NOTICES.

Catalytic Action. By K. George Falk. Harriman Research Laboratory, Roosevelt Hospital, New York. 165 pages and index, 8vo. The Chemical Catalog Company, New York, 1922. $2.50 net.

In this compact and neatly printed volume the author has collected a large amount of information upon one of the most puzzling problems of chemistry. The terms "catalysis" and "catalytic" were introduced by Berzelius in 1836. A portion of Berzelius' essay, in which he discussed this class of phenomena and suggested the terms, is quoted in the introductory chapter and makes interesting reading. The reactions that he studies covered a large range, such as the transformation of starch under the influence of acids, the decomposition of hydrogen peroxide in alkaline solution by several substances, and the production of ether by the action of sulphuric acid on alcohol. It is worth noting that four years before Berzelius published the paper, Döbereiner had called attention to the remarkable power of a small amount of manganese dioxide to cause the decomposition of potassium chlorate at a low temperature, and that the manganese compound undergoes no appreciable change. Berzelius spoke of catalysis as a "new force," but stated that he did not regard it as wholly independent of electrochemical affinities, being, he thought, merely a new manifestation of the same, but provisionally designating it by a special term. He, of course, with the information then at hand, found catalytic action more often manifested in organic than in inorganic reactions, and suggested that many of the processes of living organisms were of this nature. We know now the wide influence that catalysis has in life processes, and also many instances in non-living matter. The author calls attention to the fact that in Berzelius' time the concepts of "force" and "chemical affinity" were not the same as those attached to these terms today, but the criteria, which the Swedish chemist applied to determine whether a given action is or is not catalytic, are essentially those now employed.

The book is devoted to the consideration of catalytic action from the point of view of modern physical chemistry. It is not a manual of practise, but of theory. The author is well known for his wide acquaintance with the field both in theory and practise, and has, in the present essay, devoted himself to the elucidation of the complex conditions manifested in catalytic actions, of which so many instances and such variety are now known. He lays especial stress on Ostwald's principle that a catalyst is essentially a substance that accelerates a reaction, rather than causes it. Presumably, by this is meant that a perfectly sterile solution of pure sucrose in pure water would in time be converted into invert sugar, but the introduction of a small amount of invertase brings about the change promptly.

It has long been known that catalysts, especially the organic forms, require specific conditions of temperature and reaction for their operation. The views concerning hydrogen-ion and hydroxyl-ion concentration have found important applications in this field. The total acidity or alkalinity, measured by ordinary titration, does not supply the data necessary to determine the true reaction of the liquid to the catalyst or to the other organic materials, living or non-living. Much information on this phase of the question is given in the book.

Distinction is made between catalysts formed by living cells and those not so formed. The familiar term "enzyme" is applied to the catalysts originating in living organisms. The great part that these play in the phenomena of growth and development of all forms of life has been long evident, and research is constantly adding other instances. It is a question, however, whether there is any use in making this distinction. The word "catalyst," coined with the laudable intention of providing a term for an important class of phenomena, fell somewhat into disrepute, because often used as cover for ignorance, but it is now rescued from such condition, and may take its place among the reputable terms of science. An effort was made to set aside a termination as an indication of the catalytic function, namely, the use of the syllable "ase." Falk does not seem to be in sympathy with this for he speaks of "emulsin," "trypsin," etc. This is in accordance with the custom of many authors of chemical and physiological text-books, but it is to be regretted that the simple nomenclature has not been generally adopted. Falk does, however, use the termination in some cases, speaking of lipase, lactase and other similar substances. The spelling "sulfuric" and cognate forms, that has been a feature of the publications of the Chemical Catalog Company, is retained, but it is unfortunate that the other and even more useful reforms, suggested years ago by the Chemical section of the A. A. A. S., have not prevailed, and that American chemists, pharmacists and physiologists seem to have got cold feet on the issue of simplifying English spelling.

A special chapter is devoted to the "Chemical Interpretation of Life Processes." This is the most fascinating and important phase of human study, but while the chapter contains a large amount of information and shows a diligent and appreciative study of the literature, with ingenious interpretations of the phenomena, it does not seem that the secret of life is disclosed. The organic catalysts (enzymes, of our author) have some resemblances to living matter, and the present reviewer, many years ago, suggested that they may be considered as the connecting link between the non-living and living forms. They require certain conditions for actions and may be restrained by conditions that do not seem actually to destroy them.

The closing chapter, on "Contact Catalysis," presents an elaborate discussion of effects that have extensively applied in industrial chemistry, such as the action of platinum in the manufacture of sulphuric acid, and of some metals in the hydrogenation of oils. The latest developments of physical chemistry have been brought to bear in the elucidation of these phenomena. The work is a most valuable contribution to the literature of a subject that, in spite of the extensive investigation to which it has been subjected, seems yet but superficially developed. Each research but indicates more problems:

"Hills peep o'er hills, and Alps on Alps arise."

HENRY LEFFMANN.

THE OUTLINE OF SCIENCE. A Plain Story Simply Told. Edited by J. Arthur Thomson, M. A., Regius Professor of Natural History in the University of Aberdeen. 296 pages, 40 colored plates and 800 illustrations, 4to. In four volumes; volume one. G. P. Putnam's Sons, New York, 1922. Price $3.75 per volume.

"Boy, page Mr. Bryan." Surely the great American Commoner, who is going up and down the land denouncing Darwin and all his works, should read this book, though it is not likely he would be convinced of the error of his ways, notwithstanding the immense array of data in support of evolution which it presents. This is the first of a series of four elaborately prepared volumes, intended to bring to the public at large a knowledge of the results and theories of modern science. The author is capable of the task, as shown by his previous work, and as well exemplified in the text at hand. The bulk of the present volume is taken up with a presentation of the theory of evolution of organized beings, the author being evidently an implicit believer in the same. The first fifty pages are devoted to a summary of the modern investigations in astronomy, after which nearly two hundred pages are devoted to an exposition of the nature and causes of evolution. Man's poor relations are owned without hesitation, and as the present storm of opposition to the teaching of evolution in schools and colleges is most intense in reference to the "descent (or ascent) of man," Professor Thomson's views lead to the storm-centre. Mr. Bryan has said that he would have no particular objection to the teaching of the principles of evolution as applied to rocks and plants, but for the danger that such views would be extended to the higher organisms. Scientists may smile at such statements, and the reviewer may be criticised for deeming them worth notice, but, as a matter of fact, a large mass of the public, even the somewhat enlightened public, is easily aroused by charges that a scientific doctrine may threaten prevailing faiths, and Mr. Bryan is a powerful speaker, who has an immense vogue throughout the United States. An act, which he actively advocated, to forbid the teaching of "Darwinism, atheism, agnosticism, and evolution as applied to man" failed by only one vote in the lower house of the Kentucky legislature, and the propaganda is going on continually.

The challenge is made in the title of chapter V, "The Ascent of Man." Darwin's "Descent of Man" is credited with practically closing the discussion in favor of a direct relation between human beings and apes. It is not necessary to take up the arguments in detail. They have been before the world for many years and set forth in many phases. Professor Thomson, in common with most naturalists, emphasizes the *resemblances* of the existing apes to man, while the opponents of the evolutionary view emphasize the *differences*. It is, therefore, difficult to bring the disputants to a common ground. The discussion has been complicated by some leading naturalists making rash statements. Such are claims for restoration of heads of primitive man in which it is to be feared that the artist has been allowed too free play.

Turning to the book in hand, one notes at once a sumptuous make-up that will go far toward securing popularity. This is a wise plan; the general reader must be drawn to scientific literature by attractive setting. If the propaganda is to be conducted by lectures, these must be well illustrated by experiments or lantern demonstrations; if by books, these must be well supplied with pictures. The high development to which both ordinary illustrations and those in color have been brought in late years, renders it easy to cater to the popular desire. The present work meets all requirements in this respect. The illustrations are numerous and of high type. One can almost read the book by looking at the pictures. The type is large and clear, making it easily read, and the printing and paper first-class. The text is well written, shows a large amount of research, and an earnest desire to present the facts, though it is not possible to overlook the evidence of the author's bias towards the most advanced of the modern views. He is not to blame for this, for contact with organized structures, especially in their natural associations, leads an analytic and enfranchised mind in only one direction, namely, that a "blood relationship," so to speak, exists between them. Evolution does not necessarily involve the belief that all living organisms are of common ancestry; there may have been independent origins of life, but the similarity of plan seems to have no other explanation that the scientist can accept except the influence of heredity modified by environment.

In reading books of this type, the question arises as to whether they accomplish the purpose for which they are produced. There is a demand for them on behalf of a limited portion of the public, but the masses remain untouched by the methods and results of science. A part of the effort at the popularization of science is due to the desire to make the path of the research worker more easy, to secure a wider interest in his labors, and to justify the appropriation of public money for purely scientific investigation. Yet, even the most valuable results do not influence the minds of the great mass of the community, which clings obstinately to its folk-lore and superstitions. It is interesting to place Doctor Thomson's book alongside of the recent work of Seligman on the "Evil Eye," in which several hundred pages are devoted to setting forth the distribution both in space and time of this terrible superstition. The truth is that the mass of scientific research flows over mankind with about the same effect that the water of a stream flows over the pebbles scattered along its channel, disturbing a few, smoothing and rounding others, but leaving the general conditions comparatively unchanged. "Constant dropping will wear away the stone," but investigation shows that turbid water is most effective in this respect, and writers of fiction and poetry can swerve men more easily than can the scientist. Nevertheless, books of this class have their value, and the one now in hand is one of the best of the recent efforts to give the "man in the street" some knowledge of the accomplishments and theories of modern science.

HENRY LEFFMANN.

DYES CLASSIFIED BY INTERMEDIATES. B. R. Norris Shreve, in collaboration with Warren N. Watson and A. R. Willis, Chemists, U. S. Tariff Commission. 631 pages, including a glossary of dye-names, formula index and a key-list to Schultz numbers, 8vo. The Chemical Catalog Company, New York, 1922. $10.00 net.

The dye problem is the most complex one in the relations of chemistry to economic conditions. The enormous growth of the industry along comparatively narrow chemical methods, and yet the great variety and importance of the products make a comprehensive statement of even the leading features very difficult. The war brought to the notice of the world, and indeed, to some nations, very forcibly and painfully, the wide field that the applied chemistry of the tar-products covers. The prominence that colors and explosives have had of late years has thrown into the shade the other derivatives of the cyclic compounds, especially the medicines. While it is unfortunately true that a great many of the so-called synthetic medicines that Germany poured onto the world during the past quarter of a century were of little real value, indeed, often worthless, sometimes harmful, yet a few, such as the remedy first announced as "606," have been valuable additions to therapeutic armament. Then we have the fairly numerous and useful photographic developers, among which metol and hydroquinone are easily first in favor. Lately a color, phenosafranin, has found a useful application in photography, as it has the power to diminish the sensitiveness of the exposed plate without appreciably affecting the latent image.

The work in hand is limited to the dyes, and is mainly intended to furnish a classification according to the intermediates from which they are derived. This method is based, according to a statement in the preface, upon the experience of the factory; it does not, at first thought at least, seem to the general chemist as very satisfactory, but it is not infrequent that the manufacturer has a decidely different viewpoint from the user or the analyst. It is, however, not to be doubted that the book will be useful to the research chemist. It contains a very large amount of information well arranged. There is much information as to the importation and home manufacture of the materials. These data will be of service in elucidating some of the complex issues that have arisen in connection with the efforts to secure strong protection to the infant dye industries in this country. Much feeling is apparent in the matter; lately in Congress some members nearly came to blows. The strongest argument for national development of the dye industry is its close relation to the production of modern explosives, asphyxiating gases and other accessories of "Christian" warfare, as it is now often called. This is not the place to enter on a discussion of the economic phases of the question, the real interest being in the character of the book under review.

The work is very comprehensive, but naturally not exhaustive; the field is too large for the compass of even several volumes. The intermediates are arranged alphabetically, with abundant cross references, and with synonyms. The nomenclature is not exactly that of *Chemical Abstracts,* but the names used by that publication are given also, and the principal formulas are listed in a convenient manner, so that the use of the *Chemical Abstracts* will be made easy. A formula index to the intermediates is also furnished and a reference to Schultz's numbers. Many structural formulas are given, and it is gratifying to see that the correct method of using the benzene ring is followed.

Turning over the pages of the book one is almost awe-struck by the multiplicity and complexity of even the intermediates, and realizes the service in interpreting their structure that was rendered by Kekulé's suggestion of the benzene ring. A further emotion of awe, or even terror, seems to be capable of being aroused if one was to attempt to develop a comprehension of the character of the molecule of one of the more complex intermediates so as to include the ideas of atomic and molecular structure now so extensively promulgated by the physical chemists.

During the last eight years, the attention of American chemists has been strongly directed to the theory and applications of the coal-tar derivatives. Much has been accomplished towards securing independence of Germany. Many colors are now made of as good quality as those from east of the Rhine, and brilliant success has also attended American efforts to produce certain medicines, but the references to the literature still show how large is the world's indebtedness to Germany, and German chemists may still hold important secrets in all the departments of the utilization of tar.

The book is an excellent piece of work, shows the high mechanical execution of the publishing house that issued it, and the labor that the author and his collaborators have given to its production.

HENRY LEFFMANN.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS. Report No. 125. General Classification of Instruments and Problems including Bibliography, by Mayo D. Hersey. 22 pages, quarto. Washington, Government Printing Office, 1922.

This report is intended as a technical introduction to the series of reports on aeronautic instruments. It presents a discussion of those subjects which are common to all instruments. In the first place, a general classification is given, embracing all types of instruments used in aeronautics. The arrangement of information dealing with these various instruments throughout the reports is then briefly indicated as a guide to the reader. Finally, a classification is given of the various problems confronted by the instrument expert and investigator. In this way the following groups of problems are brought up for consideration: First, those of mechanical design; second, human factor; third, manufacturing problems; fourth, supply and selection of instruments; fifth, problems concerning the technic of testing; sixth, problems of installation; seventh, problems concerning the use of instruments; eighth, problems of maintenance; ninth, physical research problems. This enumeration of problems which are common to instruments in general serves to indicate the different points of view which should be kept freshly in mind in approaching the study of any particular instrument.

Report No. 130. Oxygen Instruments, by F. L. Hunt. 23 pages, illustrations, diagrams, quarto. Washington, Government Printing Office, 1922.

This pamphlet contains an account of the physiological effects of the lack of oxygen at high altitudes and the amounts required to be supplied artificially to aviators under normal conditions of flight. It describes in detail the various types of aircraft oxygen apparatus which have been designed and used not only in this country, but also in England, France, and Germany. Instruments of both the compressed oxygen and liquid oxygen type are considered.

Methods of testing oxygen apparatus used at the Bureau of Standards are also fully described and the quantitative results of tests of sample instruments of different types are given.

Report No. 144. The Decay of a Simple Eddy, by H. Bateman. 7 pages, quarto. Washington, Government Printing Office, 1922.

The principal result obtained in this paper is a generalization of Taylor's formula for a simple eddy. The discussion of the properties of the eddy indicates that there is a slight analogy between the theory of eddies in a viscous fluid and the quantum theory of radiation. Another exact solution of the equations of motion of a viscous fluid yields a result which reminds one of the well-known condition for instability in the case of a horizontally stratified atmosphere.

PUBLICATIONS RECEIVED.

Dyes Classified by Intermediates: Dyes tabularly arranged under each intermediate, with statistical and other data for both dyes and intermediates. Glossary of dye and intermediate names alphabetically arranged by R. Norris Shreve, Consulting Chemist in collaboration with Warren N. Watson and A. R. Willis, Chemists, U. S. Tariff Commission. 631 pages, 8vo. New York, Chemical Catalog Company, Inc., 1922. Price, $10.

Catalytic Action, by K. George Falk. 172 pages, 8vo. New York, Chemical Catalog Company, Inc., 1922. Price, $2.50.

The Outline of Science: A plain story simply told. Edited by J. Arthur Thomson, Regius Professor of Natural History in the University of Aberdeen. In four volúmes, volume one. 296 pages, illustrations, 40 colored plates, quarto. New York, G. P. Putnam's Sons, 1922. Price, $3.75 per volume.

Electrical Engineering Testing: A practical work on continuous and alternating currents for second- and third-year students and engineers, by G. D. Aspinall Parr, M.Sc., M.Inst.E.E., A.C.G.I. Fourth edition revised and enlarged. 691 pages, illustrations, 8vo. New York, E. P. Dutton and Company, 1922. Price, $8.00.

Électricité atmospherique, par B. Chauveau. Premier fascicule. Introduction historique. 90 pages, 8vo. Paris, Octave Doin, 1922. Price, 10 Francs.

Rayonnement et Gravitation, par Felix Michaud. 63 pages, 8vo. Paris, Gauthier-Villars et Cie., 1922. Price, 6 Francs.

L'Erreur de M. Einstein l'inacceptable théorie, L'Ether et le principe de relativité, par Marcelin Dubroca. 49 pages, 8vo. Paris, Gauthier-Villars et Cie., 1922. Price, 4 Francs.

Éther-Électricité-Relativisme, par le General Chapel. 40 pages, 12mo. Paris, Gauthier-Villars et Cie., 1922. Price, 2 Francs 50.

Les Preuves Astronomiques de la Rélativité, par E. Esclangon. 27 pages, 8vo. Paris, Gauthier-Villars et Cie., 1922.

[The theory of relativity leads to a certain number of astronomical inferences which are at present under consideration. The author decides that the confidence which is generally given to these data is still not wholly justified, but expects that solutions of the problems will be obtained in the near future.]

National Advisory Committee for Aeronautics: Technical Notes No. 96, Notes on Propeller Design, IV. General proceeding in design by Max M. Munk. 9 pages, plate, quarto. No. 98, Notes on the Design of Latticed Columns Subject to Lateral Load, by Charles J. McCarthy. 18 pages, illustrations, diagrams, quarto. No. 99, Notes on the Standard Atmosphere, by Walter S. Diehl. 9 pages, quarto. No. 100, Theory of the Slotted Wing, by A. Betz. 13 pages, illustrations, quarto. Washington, Committee, 1922.

U. S. Bureau of Mines: Bulletin 207, The Analytical Distillation of Petroleum and its Products, by E. W. Dean, H. H. Hill, N. A. C. Smith and W. A. Jacobs. 82 pages, illustrations, plates, 8vo. Washington, Government Printing Office, 1922.

The Piezo-electric Resonator, by W. G. Cady, Wesleyan University, Middletown, Connecticut. 32 pages, illustrations, 8vo. Reprinted from the Institute of Radio Engineers, volume 10, April, 1922.

CURRENT TOPICS.

Reconstruction Hospital. (*Industrial Management*, June, 1922, p. 362.)—Care and after-treatment of the 1,000,000 or more yearly cases of injuries received by workers while at their trades are problems giving growing concern to leaders of industry all over the United States. The condition presents both human and economic factors. Not only has the workman a right to the most modern and scientific treatment of his injury, but the industry also, no matter what it is, can ill afford to face a condition wherein he passes a long convalescence and in many cases becomes a cripple unable to take his place at the work he likes and for which he has been trained.

Various of the great industries had worked out plans of many sorts for local care and rehabilitation of their own industrial casualties before the war, and since then have applied the discoveries and lessons learned during that period to their local problem in so far as they can.

Perhaps the most sensational advances have been made in the creation of a series of strange gymnasium appliances, which give the patient by mechanical means an easy road to the recovery of all his lost control over stiffened joints and partly paralyzed muscles. All of these things take a big hospital equipment and the services of a specially trained staff of specialists. The modern science of human physical rehabilitation is new in that it has only since the war been developed to a stage where it has been possible for a whole hospital to specialize intelligently and successfully in making injured workers, who have been "cured" into alert, active, efficient men who can go back to their jobs with confidence and without pain.

One difficulty in the spread of this work is the lack of trained staffs and of nurses educated in dealing with the reëducation and rehabilitation of men who have progressed beyond the scope of a general hospital. In the matter of diagnosis alone the surgeons at the Reconstruction Hospital in New York City put the patient through a searching examination that sometimes employs the services of many specialists aided by advantageous electrical and mechanical agencies.

From this hospital they send the industrial casualty back to a job and his opportunity to again support himself and family in from one-third to one-half the time he would otherwise need. Often they send him back in perfect command of himself when he might otherwise have remained helpless all his life. R.

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AUTOMATIC TRAIN CONTROL.*

BY

FRANK J. SPRAGUE, D.Eng., D.Sc.

President, Sprague Safety Control and Signal Corporation, New York City.
Franklin Medalist, Member of the Institute.

In view of the great awakening of public interest, and especially because of existing laws and the recent action of the Interstate Commerce Commission of the United States, perhaps no time is more opportune than the present to discuss the subject of automatic train control, or as I prefer to call it, auxiliary train control.

More than two years ago Congress approved a bill which, in turning the railroads back to private control, retained for the Commission the mandatory power to order automatic train control whenever in its judgment it was justified in issuing such order.

Despite the fact that the Government took this constructive action, it is to be regretted that the power conferred was limited in character, that is, to the subject of train control, for it ought to cover the subject of safety appliances generally, such as, for example, wayside signals.

Naturally reluctant, despite disregard of recommendations made in various annual reports, to direct the wholesale installation of equipment of this character without further development and knowledge of operation, the coöperation of the railroads was

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* Presented at a meeting of the Mechanical and Engineering Section of The Franklin Institute held Thursday, April 27, 1922.

(Note.—The Franklin Institute is not responsible for the statements and opinions advanced by contributors to the Journal.)

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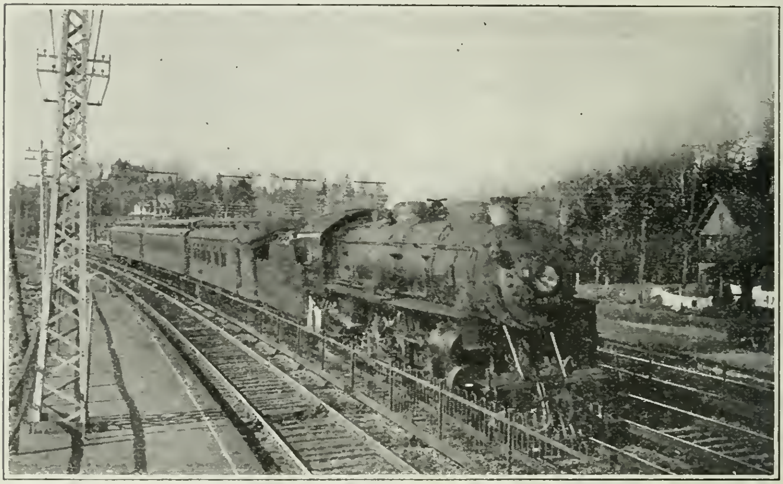
invited, to the end that a committee was appointed by the American Railway Association to coöperate with the Bureau of Safety.

Apparently, however, because of slowness of progress and a growing conviction that some act more radically constructive than the deliberations of committees was necessary, the Commission, on January 10, 1922, directed forty-nine railroads to show cause why orders should not be issued to begin and complete, within specified time limits, installations of automatic control on typical railroads, some equipped with wayside signals and others not.

FIG. 1.



Test train on tracks of New York Central.

This order was forward-looking enough to recognize the fact that automatic or auxiliary train control was not necessarily a subordinate attachment to a wayside signal, but that for a great part of the railroad mileage still unprotected by automatic signals it was possible that new developments might make the latter unnecessary.

Public hearings in accordance with the above-mentioned order to show cause were recently held in Washington, at which the railroads concerned, collectively and individually, presented their objections to making it conclusive in the form prescribed; and later, other hearings were held at which to hear those who are devoting themselves to the solution of this problem.

That the final orders of the Commission may be modified is possible, and personally I am of the opinion that some amelioration in the times specified for selection of systems, the beginning of actual installation and the period set for completion of equipment would be in the best interests of the train control art itself, and materially conduce to safety, economy and ultimate permanence. In fact, I have so expressed myself in a brief submitted to the Commission.

On the other hand, in spite of the technical and operating objections which have been raised, it is hardly conceivable that the Commission, acting under the authority of an Act of Congress which has given it the mandatory power to do that which it believes to be in the interest of the safe and efficient operation of railroads, and having arrived at constructive conclusions based upon the accumulated experience of railroad operation, as advised by its responsible experts, will abandon the general conclusions to which it has arrived.[1]

SUMMARY OF OBJECTIONS.

The arguments presented by the railroads at the hearings held in Washington may be briefly summarized as follows: That there is a general objection to third-rail impact systems, and that as regards those which have actually been put in practice many specific troubles have developed which indicate their unreliability; that the experience with non-contact inductive systems is not sufficient to justify final conclusions; that automatic train control should be regarded simply as an adjunct to wayside signals, and therefore not to be considered until the roads are fully equipped with such, and in fact until every contributing cause of accident—including grade crossings—has been removed; that sundry tests of what may be improved systems were either under way or visualized in inventors' minds, which tests might possibly some day produce something worth consideration; that with regard to even these the railroads hoped that the Commission, even should such tests result entirely satisfactorily as regards operation, would then agree that automatic train control is unnecessary; that an acceptable system should be universally interchangeable; that train control provision would be useless for the regular equipment of a road unless all foreign equipment was likewise protected; that the capacity of a road would be materially restricted; that the cost of equipment and upkeep would be prohibitive; and finally, that poverty, even at a time of coming prosperity, would not warrant any general expenditures for this purpose.

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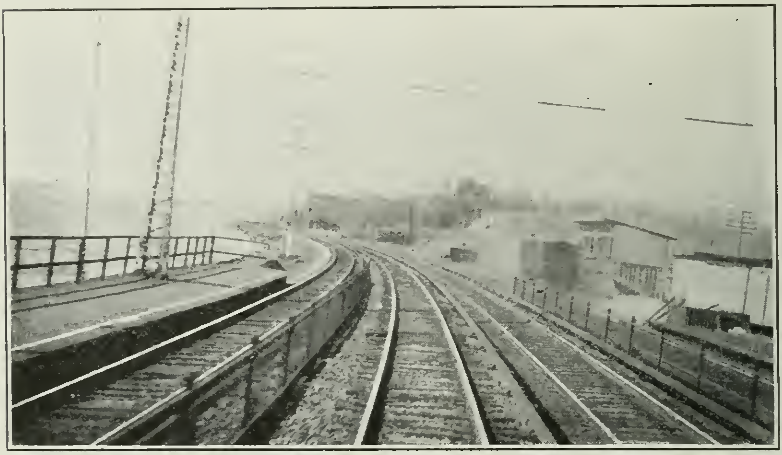
[1] The conclusions reached by the Commission, after full consideration of the various arguments advanced, were formulated in a general order issued under date of June 13, 1922, to the railroads mentioned in its preliminary order. This in the main carries out the original intention—that is, directs that the railroads shall, without unnecessary delay, proceed with the installation on a large scale of automatic train control of some character.

The time of selection of systems, as well as that for completion, was extended six months, and the privilege granted, where divisional installation had already been undertaken, or where there could be a consolidation of tests on divisions using common equipment, to proceed on that basis.

FIG. 2.



Section of test track, New York Central.

EARLY ATTITUDE.

When the general bill was in conference the statement was made that no automatic control apparatus had been developed that would meet the specifications of the American Railroad Association, and it was doubtful if there ever would be—the opinion being also expressed that "it was an utterly impractical scheme," which would remove the responsibility of handling the train from the engineman.

The same profession of impossibility of engineering accomplishment has steadily opposed every radical improvement in railway equipment and operation; in the face of which the air brake has been developed, the car stove has been discarded, the automatic coupler has been prescribed, the automatic block signal system has been installed, and steel cars are taking the place of wooden ones; while grade crossings, despite the prophecy of bankruptcy by the head of one of the most important roads entering Chicago, have been abolished in that city.

The pronouncement that automatic train control would remove the responsibility from the engineman and be productive of more serious accidents is simply an opinion. It is not supported by experience with the installations already made, whatever their shortcomings, and I believe utterly mistakes the psychology of an engineer operating under a proper system.

On the contrary, I feel certain that automatic train control—not an automatic "stop"—whether used independently or in connection with wayside signals, which are in fact themselves automatic and take the place of direct visual study of track conditions, will not only safeguard trains from collisions in case of inability of the engineer to see, understand and obey his signals, and from dangerous speeds on curves and cross-overs, but will tend to make him even more alert and efficient in his duties than at present.

THE GENERAL SUBJECT.

With the presentation of some lantern slides later, I will briefly touch upon the general subject of automatic train control, state what I believe should be the underlying fundamentals to be followed in its development, and describe something of the Sprague system in its progressive possibilities of application, and especially as illustrated in its most complete form on an installation which for some time has been undergoing intensive tests on the New York Central Railroad.

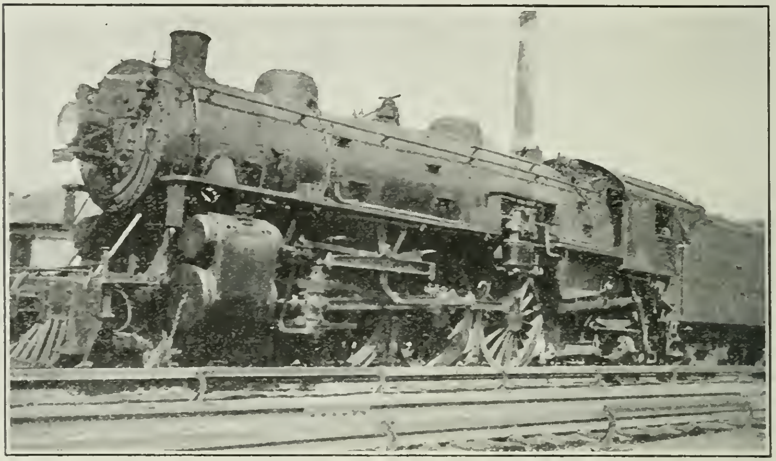
Much has been heard about the "infancy" of the automatic train control art, of the need still of years of development in "practical" railroad service; and likewise of the perfection of the wayside signal—of its reliability, the infrequency of failure, its importance and necessity as an adjunct to railroad operation, despite the fact that it is used on less than three-tenths of the mileage of the country.

As to the first, I have heard many similar views in the course of the past two-score years, during which period we have seen a large number of major electrical developments, many of which I have been fortunate enough to be concerned with.

THE WAYSIDE SIGNAL.

As to the wayside signal, heralded as the finality in operative direction, is anything the matter with it, and if so, what? Granting all that may be said of it, why hasn't it stopped railroad collisions? The trouble isn't with the wayside signal itself; but it is nothing more nor less than a limited indication of traffic conditions, and to be effective it must be seen, understood and obeyed by the engineer. The accidents which have occurred cannot, happily, be charged as a rule against failure *per se* of a system which has been elaborated with great skill and at large expense, and has undoubtedly aided materially in increasing the safety and capacity of railroad operation, or to lack of conscientious and able supervision of an intricate system by capable men.

FIG. 3.



Test engine.

It is the human element necessary to make it effective which fails—oftentimes because of no fault of the engineer but because of climatic or other causes affecting visibility. Even when seen the signal is not always understood, and, as has been well proven, it is not always obeyed even when seen and understood, for causes which, whether mental or physical, are thoroughly well known and which afford identical reasons for failures in many other human operations. If accidents occurred every time an engineer passed a red signal there would be an alarming redundancy, for any one with a modicum of experience knows that such occurrence is comparatively common.

The function of train control is to prevent such lapses, such human failures, and remove them from the causes of accident; and, in the inevitable logic of things, that which was originally designed to supplement and to enforce obedience to wayside signal indications will be developed so that the cab signal with automatic braking will in a large measure simplify, or take the place of and remove the necessity for, the wayside signal. No single feature of the Commission's proposed order is more pregnant with meaning than the recognition of this possibility.

EARLY FAILURES.

Reviewing the developments of train stops and train control, it is only fair to the railroads to say that many of the proposals advanced have been but the hasty outcropping of illy-considered and hair-brained projects by inventors whose paucity of knowledge of signal and braking systems and practice, as well as railroad operation, is only equalled by a supreme confidence in their devices as universal cure-alls for railroad ills.

But in these latter years there have been many conscientious and able attempts to solve the admittedly difficult problems of auxiliary train control, to meet the increasing demands of railway transportation, and millions of money have been spent, not always wisely, in furthering projects which gave some promise, and have achieved a measure, of success.

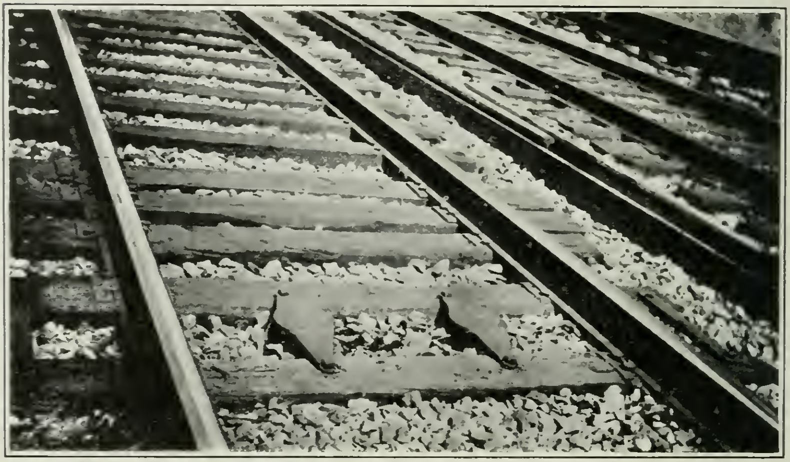
To make the path of progress a little more thorny, various arbitrary requirements have been laid down from time to time as either desirable or essential to automatic train control, some of them confessedly specified in the expectation that success would be made extremely difficult, if not impossible.

The resulting picture was a combination of infallible character which should comprise all the virtue and none of the defects of the ablest operating intelligence of a super-man, signal equipment of undoubtedly chastity and a brake system guiltness of lapses of mechanical morality, regardless of the fact that what is required is not an automaton in the place of an engineman, but an auxiliary system of train control which, while fully protecting the train and reënforcing the engineer's intelligence, would leave him practically undisturbed in the handling of his equipment so long as he performed his duties.

WHY GREATER PROGRESS HAS NOT BEEN MADE.

But the fault has not been entirely with the inventors, who have tried, however ineffectually at times, to respond to a pressing need in railroad operation. The responsibility for failure to make greater progress than has attended this development must be laid in considerable measure to the attitude of some of those in position of authority who have successfully discouraged all forward-looking efforts.

FIG. 4.



Brake application magnet.

Most of those who have been loudest in their expression of disbelief in the possibilities of auxiliary train control simply do not know the facts; and, whether because of technical shortcomings, lack of time, or absence of financial backing, many inventors have been unable to solve the problem. Some of the objectors not only have made no individual contribution to its solution, but they have been inclined to ridicule what has been done constructively by those who have given intensive study to the subject. They have been wont to revel in the difficulties of railroad operation and to surround it with a cloak of mystery, while assailing the mind with statistics, which, after all, may be most misleading.

THE SOLUTION OF THE PROBLEM.

I am not in entire accord with suggestions frequently made that the development of train control is the province of the operating officers of the various railroads, with their many conflicting ideas and practices as to signal equipment and responsibilities for train operation, but rather, as in the progress of signalling and braking, it is a problem to be developed along catholic lines in such a fashion as to marry together any kind of wayside signal, automatic or manual, or any fundamental method of indicating traffic conditions, with any kind of brake equipment, so as to satisfactorily meet the varying conditions of operation imposed by different train make-ups.

Operating officers must leave experimental work to others who, with ample means, can devote their whole energy and time to new accomplishments, and their attitude should be that of constructive critics. They can, of course, be of the utmost value and usefulness in that rôle, and their active and cordial coöperation is vital to final success.

Freely admitting, as one must, the justice and constructive value of many of the criticisms, even against operative systems, by those in authority, and also the compelling necessity of many of the requisites which have been enumerated, I am of the opinion that there are other possible characteristics which rank of at least equal importance with the majority of them, a fact which the report of the Automatic Train Control Committee of the late National Railroad Administration seems to emphasize in its comments upon speed control, to say nothing of the operative demands which alert critics have imposed upon my own developments.

GENERAL REQUISITES OF TRAIN CONTROL.

We have, therefore, adopted certain basic requisites which seem fundamental for the highest measure of success in meeting the increasingly difficult conditions of the railroad operation.

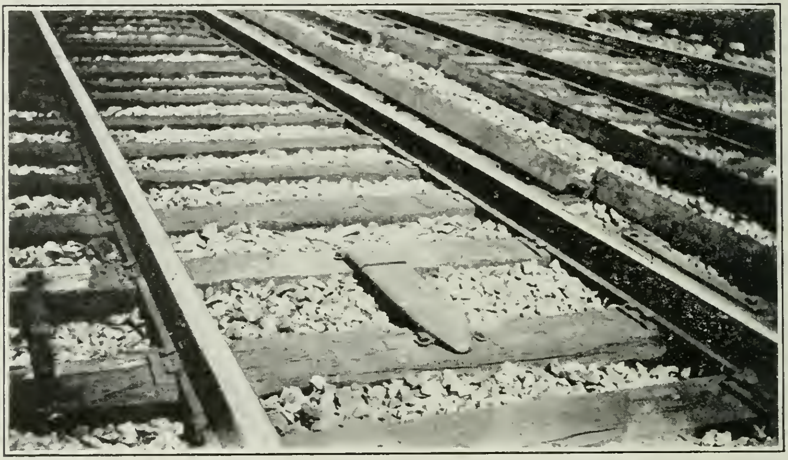
Specifically, a system should:

Be applicable to any single or multiple track railroad, with or without automatic signal equipment; and in the case of the former, regardless of whether AC or DC normal danger or normal clear signals are used, with or without interlocks and overlaps.

Be suitable for any road, regardless of the kind of power used, whether steam or electric; and in the latter case uninfluenced by the kind of current or type and location of conductors.

Not encroach upon the clearance lines of rolling stock or track equipment; or be limited by extraneous equipment along the right-of-way; or interfere or be interfered with by snow plows or dragging equipment.

FIG. 5.



Reset track magnet.

Be unaffected by climatic extremes, proof against interruption by water, snow or sleet, and subject to a minimum of depreciation.

Provide distinctive cab signals and full block protection, as reliably as any possible wayside signal.

Provide speed limitation, regardless of signals, on tangents and curves where required, and insure slowing down to safe running speeds on entering caution territory.

The engine equipment should be:

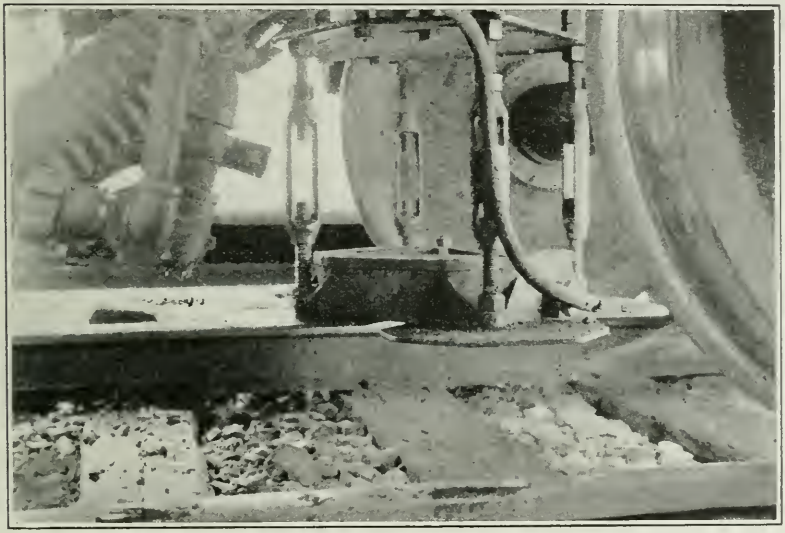
Readily applied to all types of road engines, passengers and freight, and once installed be a matter of no concern to the engineman as to adjustment, upkeep or replacement.

Unaffected by shock, jar and vibration, and proof against roadway dust and changes in atmospheric humidity.

Readily replaceable, at least as easily as the standard parts of the regular brake equipment.

Of such character that a locomotive can be used interchangeably on all kinds of train service, and with any kind of braking which may be required.

FIG. 6.



Magnetic receivers in place.

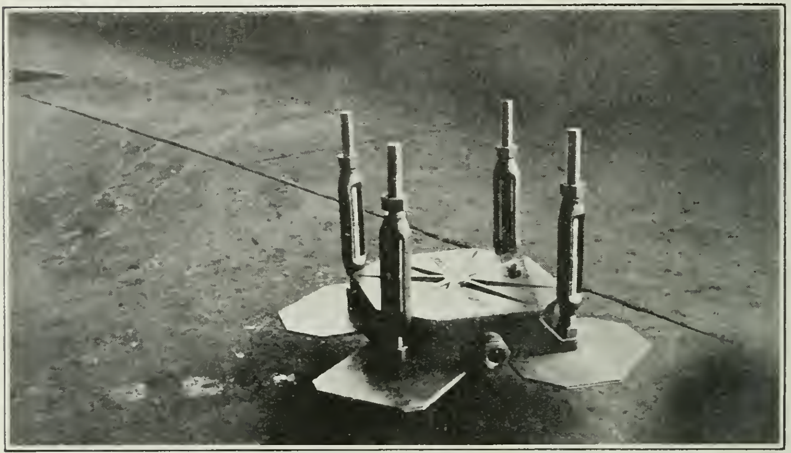
Subject to speed control, that is, to a proper coördination of the elements of train speed and braking power of equipment.

Engine and track equipment should be as nearly as possible fool-proof, and demand the minimum of upkeep and attention, both as to time occupied and special knowledge required; and necessity for adjustments by the engineman should be eliminated.

Finally, the system should be the engineer's friendly mentor and guide, aiding, not unnecessarily opposing, him, a thoroughly reliable but unobtrusive partner in the operation of his engine, which, while at all times interposing an effective shield between him and disaster, will leave, within all proper limits, the handling of the train subject to his judgment.

I have specified a somewhat complete system, to meet the varying conditions of railroad operation, but any system should be capable of abbreviation where simpler requirements are sufficient. Yet an analysis of possible equipments will readily show the limitation of choice if satisfactory results in railroad operation are to be obtained.

FIG. 7.



Magnetic receivers dismounted.

SPRAGUE SYSTEM.

To illustrate the above system I will give a brief progressive explanation of how this intermittent non-contact system of train control may, by a suitable choice of unit elements, be made to apply to all operation traffic conditions, varying from the simplest automatic stop to complete train control.

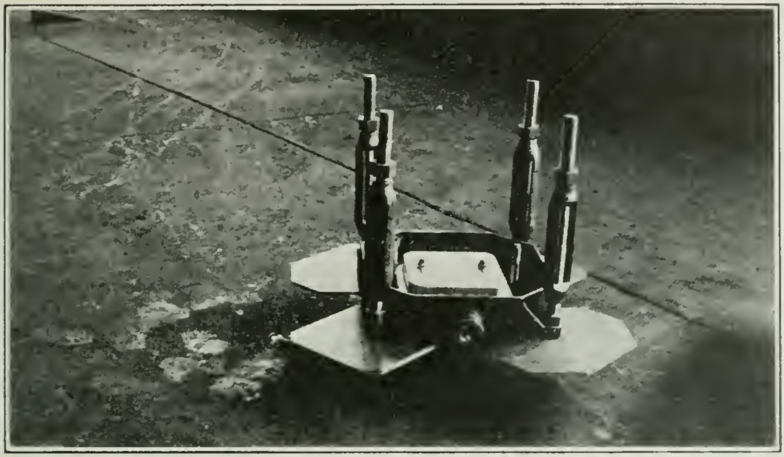
GENERAL FEATURES.

The equipment is divided into two classes:

A. *Trackway elements,* comprising one or more permanent impulse magnets carried on the ties and well below the plane of the rail heads, with means for neutralizing the active field for "clearing," under either manual or automatic control of traffic conditions, and with either hand or permanent magnet resets, or electromagnet resets controlled by traffic conditions.

All magnets are in the centre line of the track, and the brake application and reset magnets are positioned at right angles to each other, thus insuring universal registration, regardless of direction of movement or heading of locomotive.

FIG. 8.



Magnetic receivers cover off, showing floating receiver.

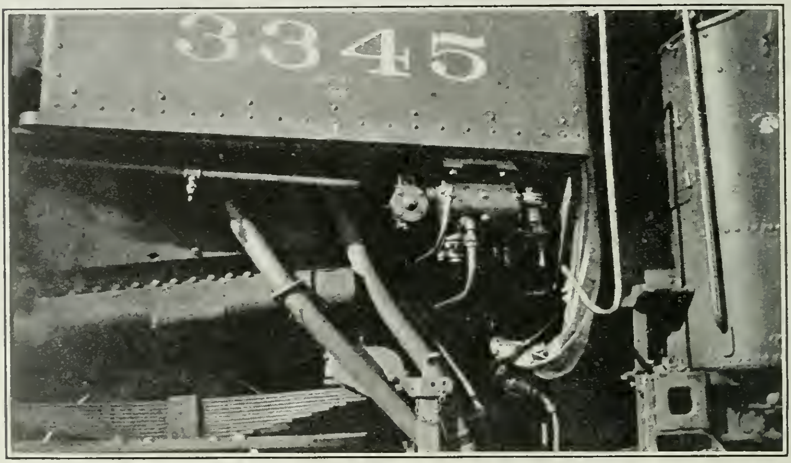
B. *Locomotive apparatus,* comprising a part or all of the following:
   A single or double magnetic impulse receiver,
   Relays and pilot valves,
   Signal lights and audible alarm,
   An interchangeable engineer's brake-head,
   Single or duplex service brake valve, with means for automatically limiting reduction of brake pipe pressure,
   Emergency valve,
   Speed-brake controller,
   Differential control valves,
   Selector and cut-off valves.

With the above units of apparatus for trackway and locomotive it is possible to assemble an equipment which will meet anything from the minimum to the maximum of traffic demands, according to the amount of protection and control required, and with, of course, corresponding variations in initial and maintenance costs.

The flexibility of this selection is indicated by the following typical illustrations:

First: *Track equipment with only one brake application magnet per block and no reset track magnet.*

FIG. 9.



Air valve assembly mounted under cab.

With this equipment there are the following possibilities:

1. *Single-impulse stop.*

In this, the track equipment of but one normally active track magnet per block may be under either manual or automatic control of traffic conditions.

The engine equipment comprises:

Single magnetic receiver,
Interchangeable engineer's brake-head,
Single control relay,
One pilot valve,
Limited service brake valve, with adjustable automatic cut-off, or, as an alternative, an emergency brake valve, the former being preferable, and
Manual reset.

This is the simplest possible equipment. The locomotive receives a single momentary initiation brake impulse when in the block in rear of an occupied block, which impulse is followed at once by a limited service (or emergency) brake application, regardless of speed. After the braking has become effective the relay and pilot valve may be restored to normal position by joint action of the engineer and fireman, and the brakes released manually. After release the train is free to be accelerated.

2. *Single-impulse stop, with low-speed limit provision.*

In this the track equipment is identical with that in No. 1, that is, there is but one brake application magnet per block, under control of traffic conditions, and there is no reset magnet.

The engine equipment is also identical with that in No. 1, except that there is added a flexibly nose-supported gear-driven speed-brake controller, the limits of which may be readily manually adjusted.

With this equipment, if the train speed has been reduced below a pre-determined limit when an active track magnet is reached the brakes will not come on, but they will become effective if the speed has not been so reduced, or is increased above this limit before the engine relay is reset. After such reset by the engine crew the train is free to be accelerated.

3. *Single-impulse stop, with automatically variable low-speed limit.*

In this the track equipment is identical with that in examples Nos. 1 and 2.

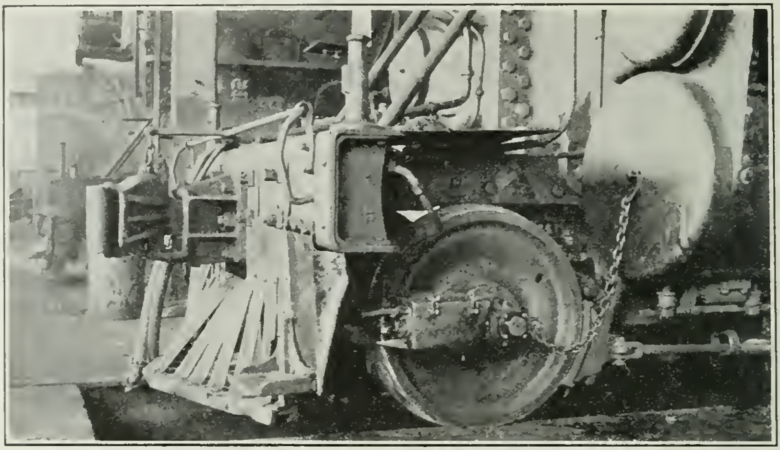
The engine equipment is the same as in No. 2, except that instead of the speed controller having only a manually adjustable low limit to which the train speed must be reduced before passing an active home magnet, it has an automatically adjusted low limit determined by a coördination of two movable parts, one responding to train speed and the other to train brake pressure, so that if the train is being properly braked on passing an active home magnet the automatic will not come on. The minimum speed at which a train may pass the track magnet is also readily adjustable. After the engine relay is manually reset by the engine crew the train may be accelerated at will.

4. *Single-impulse stop, with a two-degree alternative braking and variable speed control.*

In this, also, the track equipment is identical with that in the foregoing examples, Nos. 1, 2 and 3.

The engine equipment is the same as in No. 3, except that there is provided either a double automatic service brake valve, giving light and heavy service brake applications, with limited cut-off, or an automatically limited service valve in combination with an emergency valve.

FIG. 10.



Variable speed-brake controller.

The operation is the same as in No. 3, except that if the speed in passing an active brake magnet exceeds the maximum which is safely controllable with manual service braking equal to the primary automatic braking provided, within the required stopping distance, then the secondary braking, whether increased service or emergency, will come on.

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[2] In the above equipments it will be noted that as there are no track resets the restoring of the engine relays must be by the operation of one or more push buttons, one of which may be located outside the cab, and where two are supplied they require the coöperation of engineer and fireman.

Also, all brake impulses are single, and when once the brakes are applied they are effective to bring the train to a stop; but when the engine relays are reset by hand the train is free to proceed without limit of acceleration so far as the automatic apparatus is concerned.

In examples Nos. 2, 3 and 4, in fact on all equipments, a maximum speed provision may also be readily added, so as to provide speed limits on tangents.

The service brake valve settings are readily adjusted to any required brake-pipe reduction and corresponding brake effort.[2]

Second: *Blocks with one brake application magnet and one reset magnet, either permanent, or electro under control of traffic conditions.*

The track resets, located near the end of each block, that is, following the brake application magnets in sequence of registration, may be either fixed in character or subject to manual or automatic control of traffic conditions.

In the first case the reset simply restores any engine relay which has functioned in passing over an active brake application magnet to its normal condition when the train reaches the end of the block, regardless of traffic conditions, while in the second case the reset is effective or not according as the advance block is clear—thus enabling a train, after receiving a brake application impulse, to be held down to any pre-determined low limit of speed until it has passed over an active reset magnet, so conditioned by a favorable change of traffic conditions.

It follows that the locomotive equipment indicated in examples Nos. 2, 3 and 4 has a reset circuit operated—not by hand as hitherto described but by another track impulse. This, therefore, requires an additional impulse receiver on the locomotive, which may be either separate from the brake impulse receiver or be a composite with it.

In using a fixed track reset the new combinations of the equipment, corresponding in all other respects, except as noted, with examples Nos. 2, 3 and 4, may be designated as follows:

5. *Single-impulse stop, with low-limit speed provision and fixed track reset.*

6. *Single-impulse stop, with variable speed control and fixed track reset.*

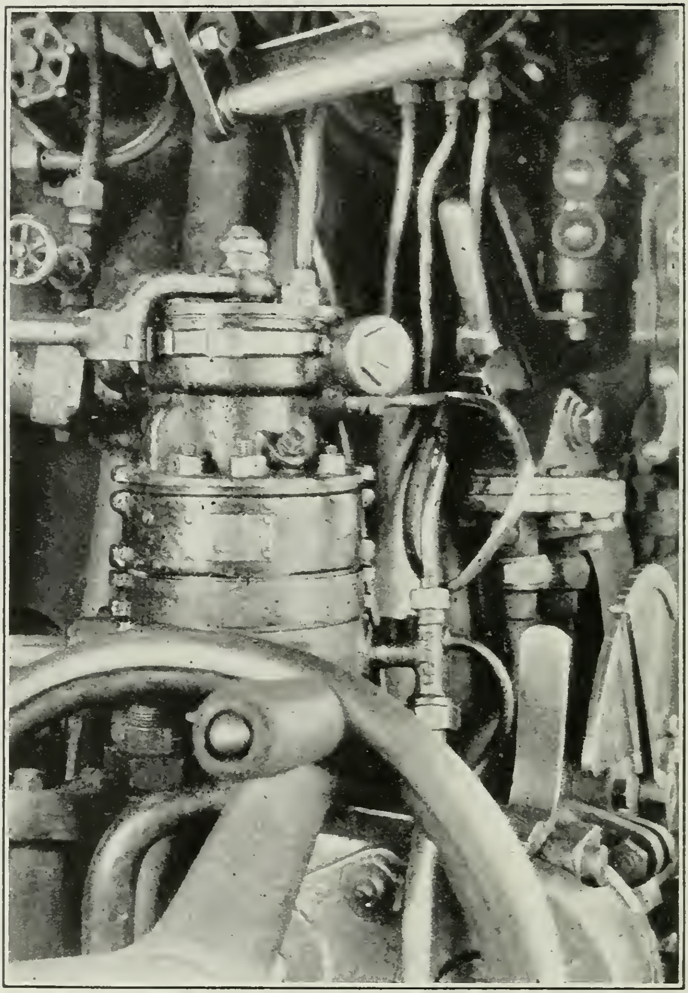
7. *Single-impulse stop, with a two-degree alternative braking, variable speed control and fixed track reset.*

If instead of a permanent track reset one under control of traffic conditions is used, then the locomotive equipments, modified as noted in examples 2, 3 and 4, will give combinations which may be designated as:

8. *Simple-impulse stop, with low-limit speed provision and traffic-controlled reset.*

9. *Single-impulse stop, with variable speed control and traffic-controlled reset.*

FIG. 11.



Main engineer's valve and signal lights in engine cab.

10. *Single-impulse stop, with a two-degree alternative braking, variable speed control and traffic-controlled reset.*

In the equipments thus far described there has been provided but one brake application track magnet per block, without or with a fixed or a traffic-controlled reset magnet; and only one brake application magnet, that in the rear of an occupied block, is under the control of that block.

It should be pointed out that the brake-application magnets are normally active, and the traffic-controlled resets normally dead, that is, both are installed on a normal danger principle, the clearing current being effective only when a train enters a block immediately in rear of an unoccupied block.

To further extend protection, still using but one application magnet to a block, but with a traffic-controlled reset, the signal circuits may insure that the brake application and reset magnets in the *two* blocks immediately in rear of an occupied block are under the control of that block.

With this arrangement, a train approaching an occupied block may receive two brake-initiating track impulses, one in the block second in rear of the occupied block, that is, while approaching a caution indication, where wayside signals are used, and another in the block immediately in rear of the occupied block.

These impulses may be termed " primary " and " secondary," and will be effective according to the kind of equipment which is supplied on the locomotive.

Where a plurality of alternative results—as will be referred to later—is not provided there will follow, according to the equipment which has been installed, either: A light limited service brake application, succeeded by a possible full service application; or, a heavy service application, followed by a possible emergency application, and the secondary braking will be under a fixed or variable speed control. The train will thus be doubly warned, and finally, if necessary, automatically braked.

With this arrangement of track magnets, if the leading train passes into its next advance block before the following train reaches the reset magnet of its own block, the engine relays of the latter will be restored to normal and only a primary impulse will be received in the following block. This combination, especially with a coördinated variable speed-brake control, is all that many railways will require.

It will be noted that any brake application magnet may be either a " caution " or " home " magnet.

To meet the above conditions the engine equipment is augmented by the addition of another relay, to provide for the proper sequence of brake impulse results and functioning of the reset.

With the above as described we have therefore an equipment which may be designated as follows:

11. *Two-block double-impulse stop, with variable speed control and traffic-controlled reset.*

On congested service, and to provide for interchangeability of locomotives for different train make-ups, a more complete engine equipment is necessary.

With this end in view, the valve assembly of the engine equipment includes one adjustable double-limit service brake application valve with automatic cut-off, and also an emergency valve. To these is added a rotary selector valve, which makes it possible, with only two brake application impulses from the track, to get a variety of results, according to the selector valve used and its setting.

For example, the first brake impulse may give either:

Simply a warning, or
Light service application, or
Full service application,

and the second brake impulse may give either:

Heavy service application, or
Emergency application.

Resulting combinations are evident, as, for example:

Warning and then a limited service application, or
Light service followed by a full service application, or
Full service followed by an emergency application.

There is, however, this limitation—that any brake application received on the first impulse may be immediately released by the engineer before becoming effective if below a pre-determined speed, but the second automatic brake application may be avoided only if the engineer insures the proper braking of his train, either automatically or manually, before reaching an active home magnet, and maintains sufficient braking until his train has been reduced to the permissible low speed for proceeding, a condition of safe procedure indicated by a yellow " proceed " light in his cab.

Violation of this condition, or having brought the train to low control speed, the train speed is increased before reaching an active reset, will cause the secondary brake application to take place. On the other hand, proper handling of the train will keep it completely under the control of the engineer.

In addition, provision is made so that if the brakes have actually come on automatically they may be released either manually from the cab, or only, after an enforced stop, from the ground in coöperation with the engineer.

The equipment thus described may be designated as:

12. *Two-block double-impulse stop, with selective braking, variable speed control and traffic-controlled reset.*

When the train service is highly congested and it is necessary to permit the maximum of train movement with full protection, each block may have two brake application magnets instead of one, which with the reset magnet are all under control of the traffic conditions of the next advance block. Both brake application impulses will, therefore, occur in a single block at shorter intervals. This combination—using the selective braking locomotive equipment specified under No. 12—may be designated as:

13. *One-block double-impulse stop, with variable speed control and traffic-controlled reset.*

The following table shows the general characteristics of these various equipments:

Scheme No.	Brake Magnets per Block.	Brake Impulses.	Resets.	Kind of Braking.	Low-speed Limit.
1	One	One	Manual	Single	None
2	"	"	"	"	Fixed low
3	"	"	"	"	Variable
4	"	"	"	Alternative	"
5	"	"	Fixed track	Single	Fixed
6	"	"	"	"	Variable
7	"	"	"	Alternative	"
8	"	"	Traf. contr.	Single	Fixed
9	"	"	"	"	Variable
10	"	"	"	Alternative	"
11	"	Two	"	Double	"
12	"	"	"	Selective	"
13	Two	"	"	"	"

Groupings.—Nos. 1, 2, 3 and 4. Single brake impulse. One application magnet per block and no track reset.

Nos. 5, 6 and 7. Single brake impulse. One application and one permanent reset magnet per block.

Nos. 8, 9 and 10. Single brake impulse. One application and one electro reset magnet per block.

Nos. 11 and 12. Double brake impulse. One application and one electro reset magnet per block.

No. 13. Double brake impulse. Two applications and one electro reset magnet per block.

COMPARATIVE ADVANTAGES OF VARIOUS EQUIPMENTS.

Of these various arrangements:

No. 1 is the simplest, but requires either an absolute stop, which would interfere with traffic, or a permissive release, which has certain objections.

Nos. 2, 5 and 8 are not as good as 3, 6 and 9, because these latter provide a *variable* instead of a *fixed* low-speed limit, and hence are more efficient, even if but one brake impulse is used.

FIG. 12.

Test train in yards.

Of 3, 6 and 9, which call for *hand*, *fixed track* and *traffic-controlled* resets, respectively, the latter, 9, is of course to be preferred.

Again, 7 and 10 are preferable to 6 and 9, because they provide for *two* degrees of braking with a *single* impulse, according to speed; and 10 is, of course, better than 7, because the reset is *traffic-controlled*.

Next, 11 is preferable to any of the preceding arrangements, because it provides for *successive impulses* in *two blocks*, caution and home, and *two degrees* of braking.

No. 12 is even superior, because by use of differential and selector valves each impulse may have either of a pleurality of predetermined results, and the variable combinations of these are such as to make the same equipment interchangeable for all kinds of traffic. This arrangement is sufficient to meet the operating conditions on a large class of railroads.

No. 13 is an alternative of 12, but only in so far as the track equipment is concerned—there being two brake application magnets in each block, instead of one, as in all the preceding arrangements, as well as a track reset; and both impulses are confined to one block, as may be required in the densest traffic.[3]

REVIEW.

Time does not permit a full description of the equipment above outlined, which has been developed largely under the criticism, and in consequence, of many exacting demands made by the operating officials of a great railroad.

It will be noted that it depends for its track impulse upon that fundamental on which are based every electric light and power plant, every electric railway, every signal system, and every compass, telegraph instrument and telephone—magnetic induction and its power to influence any conducting medium within its scope. If it may be relied upon in so vast a field we can surely use it in this particular one.

The question naturally arises: Why is it that this particular application stands almost unique in the field of automatic train control? It is simply because much had to be learned by long and costly experience as to how to meet the many conditions incident to track and engine equipment, and new practices developed to make use of fleeting impulses of small energy value. But perplexing as these at times have appeared the difficulties have been fully surmounted, with results that are in the highest degree gratifying.

The monetary impulses initiated by the passage of a train through the active fields of the normal danger track magnets, under automatic or manual signal control, having been received on the locomotive, certain static conditions are established, persistent throughout the block, which makes possible, with the same apparatus, to meet the opposing extremes of braking requirements imposed by long tonnage freight and fast passenger trains, regardless of the character of the brake equipment on the trail cars.

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[3] No. 13 is the equipment provided in the New York Central tests, but it can be readily abbreviated to illustrate any of the other arrangements.

It will provide, at the will of the management, any required combination of alarm and primary and secondary brakings, the former of measured and limited service character, and the latter, service or emergency under speed-control, and subject to the rules of the road with regard to the making of a positive stop or proceeding under control.

It will afford complete block protection, and also put a restraint not only upon the permissible running speeds in a caution block, but upon excess speeds on tangents and dangerous curves.

It need never apply uncontrolled braking if the engineman obeys his orders and the indications of his cab signals.

The impulse receivers on the locomotive equipment are replaceable as units; sealed when installed, and proof against running shock, vibration, dust and humidity.

The electric relays are likewise sealed, and the connections are made automatically. As a measure of their reliability it may be stated that the number of movements of the contact parts in the full life of a locomotive would not equal those on a " flivver " in a single day.

The speed-brake control mechanism is axle-centred, gear-driven and spring-suspended, as in my fundamental and now universally used railway-motor practice; it is likewise sealed and proof against dust and humidity.

The electric and air valves form a single assembly, much on the order of the distributing valve of the standard brake equipments, and are replaceable as a whole or in parts.

The local electrical supply on the locomotive is from a storage battery, or the headlight generator, or both simultaneously, and the battery is charged by the generator as in automobile practice.

Save for the speed-control, every part of the locomotive equipment is normally in a static condition. None of it is open to the inspection of, or requires adjustment by, the engineer. Replacements would ordinarily be periodic only, the same as obtains with the triple valves.

All parts, air or electric, of the locomotive apparatus may be readily replaced, and when removed may be taken apart and reassembled without any special tools whatever.

The readiness of the equipment for operation is automatically assured when the engine is put into operation, and cutting it out when the engine is laid up requires the minimum of manual attention, being made a function of the air brake conditions.

It will operate efficiently, regardless of the type of motive power, or the kind of current or conductors used in an electrical system; also on any combination of double-heading, with the equipment of the leading locomotive cut out or disabled, and when running normally headed or with tender first in direction of traffic on steam equipments, or with either end forward on electric equipment, as well as when pushing equipment ahead of the motive power. It will also afford protection in certain cases of disablement of a part of the equipment.

In case of failure of current supply the equipment may be rendered inactive, so that normal control of locomotive and brakes will remain, but such cut-out is self-detecting.

Neither the installation nor the operation of the train control equipment interferes in any way with the power of the engineer to augment to the limit his braking power to stop his train, and all release of brakes is manual.

All apparatus on the locomotive, as well as on the track, is installed on the normal danger plan.

Finally, the total equipment on the locomotive bulks less and is simpler than the lighting and braking equipment individual to a single trail car on a modern passenger train.

THE NEW YORK CENTRAL TESTS.

The development of the system thus outlined has been the result of large expenditures over a period of nine years, half of which is to be credited to war conditions.

Recently the Sprague Company, in coöperation with the Joint Committee on Automatic Train Control, entered into a somewhat unusual contract for an intensive test with the New York Central Railroad, which has long had this system under special study—a special committee having made a unanimous report in favor of a thorough test.

This test is ordinarily being carried on for seven hours a day, six days a week, on a section covering six signal indications on one of the incoming main tracks near New York, where there is a combination of unusual elements and from which all other traffic is temporarily excluded; and where, also, the conditions permit of several hundred recorded operations a week under varying conditions, as many, in fact, as would occur on a considerable division in normal service.

On this section are also operated heavy electric locomotives and multiple unit trains, with direct current from a third rail and traffic rail return. A normal clear AC signal system is used, while the normal danger track magnets are supplied from storage batteries maintained by a trickling charge from the AC power line.

The quite considerable costs of the tests are borne jointly by the Sprague and the railroad companies, the former supplying the engine and track equipment and the latter the engine and the observation and train cars, the necessary train crew, and the labor and material for the wayside circuits and installation.

For some months the operation of this equipment, which started its preliminary runs on February 20, 1922, will be under the supervision, at least, of the representatives of the Bureau of Safety, the American Railway Association and the New York Central Railroad Company, while duplicate written or graphic records available for all will be made of every official test.

Special tuning up of the track will permit of high running speeds when desired. The speeds already made are fully up to the maximum permitted for this section of the track.

Some lantern slides of location and equipment will be shown, to which brief reference may be made as follows:

On the Track.—In each block are situated two normal danger brake application magnets, one near the entrance end and one at the critical point in the block, and near the exit end is a differential reset magnet. In some other cases but one application magnet need be used, and normal engine conditions may be restored by hand.

These various magnets are under the control of the track relays and the signal blades, the application magnets being normally alive and the reset normally dead.

When a train enters a block in rear of a caution or clear block the application magnets are automatically cleared by a neutralizing current supplied to coils enclosing the working poles, thus permitting the magnetically responsive receiver on the locomotive to pass through the space over the magnet poles without being affected.

If the advance block is not clear then the application magnets will remain at normal danger, or active, and the magnetic receiver is subject to their influence; the reset is then inert.

The track magnets are enclosed for protection in substantial manganese steel casings, thoroughly sealed, and supported in the ballast, between pairs of ties, by extension arms resting upon and secured to the ties.

The application and the reset magnets are placed at right angles to each other in the centre of the right-of-way, thus insuring universal registration with the corresponding receivers, regardless of direction of motion or heading of equipment, and the polar faces are between four and five inches below the planes of the tops of the running rails.

On the locomotive there are:

A double receiver, composed of two pairs of flat iron collector plates, attached to the bottom of a non-magnetic box which is hung from the tender by adjustable supports, these plates being from three to four inches above the tops of the rails, making a total clearance of seven to eight inches. The greater the normal clearance provided the less the influence of unavoidable variations.

Within the box, with its locked top, is a floating continuation receiver in which is concentrated on moving armatures of small mass, which maintain normally closed electric circuits, the magnetic flux picked up by the receiver when it passes over an active track magnet. As the tops of the pole pieces are only eight inches in diameter, the time of passage when a locomotive is running at high speed is very short, say from 1/100th to 1/150th of a second, in which time a small magnetic impulse must be picked up and translated into action, while the apparatus which responds to this minute influence must be indifferent to the shocks and jars inseparable from train movement.

The Relays.—The medium to which the impulses are transmitted, and by means of which they are translated into action, comprises an assembly of three coils, operating self-centering pressure contacts, in a definite sequence, and they will readily respond to impulses as short as 1/1000th of a second. Being sealed, automatically connected, and cushioned, they are likewise proof against undue wear due to shock or vibration.

The Valve Assembly.—The impulses picked up by the receiver, and differentiated by the relays, result in influencing the action of two pilot control valves, whose function is simply to establish an opening to atmosphere of one or other of the piston chambers which control the movement of a ported valve, whose operation may at will effect any required combination of light and heavy measured service and emergency brake application, under speed control, and with or without enforced stop, or with the privilege of proceeding under limited speed until released—varying possibilities necessitated by the widely differing conditions of train make-up and operation met in practice.

The valve assembly thus briefly described is supported under the shelf of the cab, and is equally applicable to any kind of standard brake equipment. Despite its numerous possible functions it has far less parts and is simpler in construction than the UC triple valve commonly used on high-speed train equipment. Its various parts are, in many particulars, of identically the same character as other parts of the air-brake system. They may be separately removed and require only like care and attention.

Speed Control Mechanism.—This is carried on an extension of one of the forward truck axles, on which it is centred on one end, while the other end has a spring-suspended nose support. The drive is by enclosed bevel gearing, running in oil, while the governor part is carried in a dry chamber in which are also supported certain fixed and movable end-contact carbon brushes.

To the free end is carried a flexible cable, terminating in a standard coupling, and also a single flexible air hose connected to the engine brake system. The whole constitutes a combination of a speed-responsive device (not an odometer) and a brake-responsive device, by means of which the necessary coördination may be automatically secured to prevent unnecessary operation of automatically initiated braking.

The above elements constitute the external part of the locomotive equipment, except for the battery and the standard headlight generator, which are the sources of electric supply for the engine equipment, these to be used independently or together.

The remaining parts, which are in the cab, are of the simplest character. One is a manually and power-operated engineer's valve, interchangeable with the standard valve, to which air-oil pressure is delivered when a track impulse is received, to move the handle to lap position, the actual braking other than manual being assured by the automatic valves already referred to.

In addition to this engineer's valve there are two pairs of signal lamps, one on each side of the cab, which show a green light when the equipment is in running order and the block ahead is clear, and a yellow "proceed" lamp, which indicates the relations existing in the speed-brake control and hence the condition of safe procedure.

COMMENT ON CARRIERS' TESTIMONY.

Some brief comment may be permitted on the testimony presented in Washington on the subjects of cost, depreciation, capacity and interchangeability, and a specific objection which has been raised elsewhere—the possible negative result of train control in the event of an angle cock in the train pipe being closed, the cause of a grave railroad accident a couple of years ago.

With regard to this last objection, the present angle cock is a weak point in all braking systems, and hence there has been developed by associated interests a semi-automatic angle cock which promises, according to many private tests, to eliminate this weakness and make impossible the cutting-off of the power to brake a train, either manually or automatically, after a train pipe has been charged.

Pleadings which emphasize the need of universal interchangeability and completeness of equipment to make automatic train control of practical value may be plausible, but these have been many times advanced with regard to other present-day developments, and are effectually refuted, for example, by the variation in electric railway equipments, and by the fact that many roads are operating the same equipment over lines only partly equipped with automatic wayside signals.

As regards comparative operating capacity, I am satisfied that, considering all the varying conditions of visibility, cab signals with auxiliary brake control will materially increase the safe capacity of roads not now operating under automatic block signals, and where such are in use the capacity will not be restricted. The conditions under which the New York Central tests are being conducted will afford opportunity for a strict comparison in this respect, and with graphic records of performance under both conditions which cannot be disputed.

COSTS.

In the matter of cost and depreciation the opinions expressed are in the main highly fantastic, and totally lacking in that detail which would entitle them to serious consideration. The cost of installation is necessarily variable, according to the amount of protection required, the extent of existing wayside equipment, the size of the installation and the type of apparatus employed.

This cost is made up of that of three distinct parts:

Engine apparatus,
Track equipment,
Wayside installation.

The first two items may of course be definitely given, but they may only be fairly considered in connection with the question of depreciation, for the saving of even a hundred dollars a mile in the latter item corresponds, on an eight per cent. basis, to a capital equivalent of twelve hundred and fifty dollars.

It has been stated that, considering the total costs, the interest charge, depreciation and up-keep would amount to as much as a thousand dollars per annum for each mile of track equipped. The absurdity of such a statement should be apparent to anyone, and can only be excused on the ground of complete ignorance as to what has been accomplished, for after allowing liberal charges on the cost of equipment and installation there would still remain over eight hundred dollars per mile for upkeep, or the capital equivalent of ten thousand dollars per mile.

Reduction in depreciation is, therefore, of far greater moment than undue scrimping in first costs. Special effort has been directed to this matter, with such gratifying results that I know this item can be maintained well within moderate limits.

COMPARISON OF DEPRECIATION.

As an illustration of the difference, for example, between a third-rail contact device and one actuated by magnetic induction, I may cite certain approximate comparative ratios as follows:

Necessary number of movements of contacts	1 to 200
Train movement required for operation	1 to 100
Contact movement	1 to 200
Pressure on contact	1 to 5000

Rubbing contact:
    None on one, and
    Serious on the other.
Impact:
    None on one,
    Large on the other.
Exposure:
    One completely enclosed,
    The other always exposed.

In short, the depreciation of the receiver parts in the induction system is represented by a practically irreducible minimum.

A similarly low depreciation must exist with regard to sundry parts of the engine equipment, such as the relays, and to a less degree the speed-control mechanism; and as to the other parts they are of the order common to standard air-brake equipment.

The costs of wayside equipment depend upon many factors, such as the existence, or otherwise, of poles and common circuits, whether the poles are owned or leased, whether a DC or an AC signal system, or none, is used, and the kind or capacity of batteries in the former, the presence or absence of AC power lines, and so on.

The requirements as to wayside pole circuits, with the usual common return and clearing lines, are the equivalent of one conductor per signal indication, roughly per mile of double track, and the fundamentals of our track magnet circuits are elemental in character. Their application to existing circuits is a matter of ready adaptation by signal engineers, and one affording no excuse for complication or material expense.

The power used in the circuits of the track magnets for clearing them, when installed on the normal danger system, is inappreciable, for, except in a special case, current is used only when a train is passing through a block and the advance block is clear. It is a function of the number of locomotives in use, regardless of the length of the division, and according to present experience would average a kilowatt rate for from fifty to seventy-five locomotives in service, divided among all the batteries on the line—less than is required to light a single passenger car.

While the system described has been developed under my direction it would be a mistake to assume that it is the product of any single mind, for it represents an accumulation of invention and experimental work in which my various associates have played a large part, notably our Chief Engineer, Lt. F. D. Sprague. I might add that we are also deeply indebted to the criticisms and suggestions of signal and brake experts, the natural result of many intimate contacts with them.

Elementary Proof of the Form of the Caustic by Reflexion. G. CESÀRO. (*Bulletin, Section of Sciences,* Royal Academy of Belgium, No. 7, 1921.)—The caustic, "the cow's foot in the milk," is that cusped bright line found somewhat in front of a mirror of circular, not parabolic cross-section, when a beam of sunlight, parallel to a radius, is incident upon the reflecting surface. Two adjacent rays of the beam give rise to two reflected rays, which intersect at some point that is unusually bright because it gets energy from more than one ray. Let a beam of sunlight travel along the axis of a cylindrical napkin ring or of a tumbler, then tilt the object a little and the caustic becomes visible on the bottom of the tumbler or on a piece of paper across the end of the ring.

The form of the caustic has long been known, but for its derivation and investigation the differential calculus has been employed. Now Cesàro furnishes a derivation with nothing but algebra, geometry and elementary trigonometry, and all so simply explained that a good high school graduate can follow him. Would that the author might turn his talents to the elucidation of the Theory of Relativity!

With consummate art, for the article is "of a lucidity," as the French would say, we are led by easy steps to recognize that the caustic is an epicycloid. About the centre of the reflecting surface describe a circle with half the radius of the surface. Upon the radius of the reflecting surface, parallel to the beam of light and between this surface and the smaller circle just drawn, put a circle with a radius of one-quarter of the radius of the surface. This smallest circle is tangent to the surface and to the circle just drawn. This just mentioned point of tangency is a point of the caustic and is at the cusp. Now roll the little circle upon the inner circle. The point of the moving circle which was at first in contact with the inner circle describes the epicycloidal caustic as it moves away from its former contact, whether up or down.

G. F. S.

Isopropyl Alcohol.—The manufacture, properties, pharmacology, and uses of isopropyl alcohol are described by DUDLEY H. GRANT and CARL O. JOHNS (*Am. J. Pharmacy*, 1922, x-c iv, 418–425). This alcohol is a by-product of the petroleum and natural gas industry. The olefine gases, including propylene, are absorbed in sulphuric acid; and the resulting alkyl sulphuric acids are hydrolyzed with the production of alcohols. Propylene yields isopropyl sulphuric acid; and this compound is converted into isopropyl alcohol by hydrolysis. Isopropyl alcohol is readily dehydrated by a short digestion with an excess of dry sodium hydroxide, and subsequent distillation. It is more toxic than ethyl alcohol, but far less toxic than methyl alcohol. Isopropyl alcohol may be used as a dehydrating agent, an antiseptic, an antidote for phenol burns, a sterilizing medium for ligatures and instruments, a preservative for anatomical and pathological specimens, a key denaturant for industrial alcohol, a solvent in the manufacture of five chemicals, synthetic drugs, plant principles and related substances, a precipitant, and for other purposes.

J. S. H.

THE STABILITY OF ATOM NUCLEI, THE SEPARATION OF ISOTOPES, AND THE WHOLE NUMBER RULE.*

BY

WILLIAM D. HARKINS, PH.D.

Department of Chemistry, University of Chicago.

INTRODUCTION.

SINCE almost all of the books and most of the papers which have been published during the last decade on the subject of atomic structure are the work of physicists, it is but natural that the chemical facts which are of fundamental importance in connection with such a subject have been largely ignored, except in such portions of the field as have been popularized by certain chemists. During the last few years these chemists have succeeded in replacing the physicist's theory that the atom lies in a plane, by the more useful idea of Parson, G. N. Lewis, and other chemists, that it is three dimensional. These theories refer to the structure of the outer part of the atom.

Chemical facts are of prime importance also in connection with the study of the structure and stability of the innermost core, or nucleus of the atom. However, the chemical facts are so numerous and so detailed that it is difficult for physicists to comprehend them without a careful study, so they are usually disregarded, even so much so that in some cases experimental results have been published which were seemingly not in harmony with the general system revealed by such facts. In such cases later work has shown the original experimental results to be erroneous.

The chemical data which are of the most value in the study of the stability of the nuclei of atoms are the accurately determined chemical or mean atomic weights. Since it has been discovered that most elements are mixtures, and that therefore the chemically determined atomic weights are usually only mean values, there has been a tendency to minimize the importance from a scientific viewpoint, of the determination of such values. It is the purpose of the present paper to show, so far as is possible in its limited scope, that the discovery of isotopes has made the mean atomic weights assume a place of much greater importance, since they now become the fundamental basis for studies of nuclear composition and stability. That this is true is of interest to chemical science in America, since it is in this country that the most important work on atomic weights has been carried out by T. W. Richards, and by his coworker, G. P. Baxter.

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* Presented at the Stated Meeting of the Institute, held Wednesday, April 19, 1922.

I. INTERPRETATION OF THE ATOMIC WEIGHTS.

Early in the year 1914 the writer had occasion to make a detailed study of the atomic weights of the eighty-six elements then known, and it was evident at that time that they revealed a very remarkable story: That of the building of the atoms. This took the form of several papers,[1] published in 1915, which revived the hypothesis, published just a century before by Prout,[2] that hydrogen is the fundamental substance or protyle from which all other substances are built. When first presented Prout's idea received the vigorous support of Thomson, considered in England as one of the leading chemical authorities of the day. Many years later, from 1840 to 1860, it was advocated by Dumas, who made a large number of atomic weight determinations during this period. For a time, during the first half of the eighteenth century, many other chemists, among them Gmelin, Erdmann, and Marchand, were also numbered among Prout's supporters. On the other hand, the most accurate of workers on atomic weights, Stas, who in the beginning tried to aid Dumas in the revival of Prout's hypothesis, afterward designated it as pure fiction, since he was fully convinced of this by his own extremely accurate atomic weight determinations, and Berzelius at all times adhered to the view that exact atomic weights could not be determined except by experiment.

The basis of Prout's idea was the fact that he found the atomic weights of a considerable number of elements to be whole numbers as shown in Table I.

Since, as is obvious from the table, most of the atomic weights used by Prout are very far from being correct, it is apparent that the evidence for his hypothesis was very faulty. Indeed the fact that the chemical atomic weights are on the whole far from whole numbers when hydrogen is taken as a basis, led to the rise of a strong prejudice against this idea, as is well illustrated by a quotation taken from the 1906 edition of Meyer's history of chemistry.

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[1] *Proc. Nat. Acad. Sciences*, 1, 276 (Feb., 1915); *J. Am. Chem. Soc.*, 37, 1367–1421 (June, 1915); *Phil. Mag.*, 30, 723–34 (1915), Harkins and Wilson.

[2] *Annals of Philosophy*, 1815.

TABLE I.

Prout's Table of the More Accurately Determined Atomic Weights.

Element.	Sp. gr.	Atomic weight, 2 vols of hydrogen being. 1.	Present atomic weight.
H	1	1	1.0078
C	6	6	12.00
N	14	14	14.008
P	14	14	31.04
O	16	8	16.00
S	16	16	32.07
Ca	20	20	40.07
Na	24	24	23.00
Fe	28	28	55.84
Zn	32	32	65.37
Cl	36	36	35.46
K	40	40	39.10
Ba	70	70	137.37
I	124	124	126.92

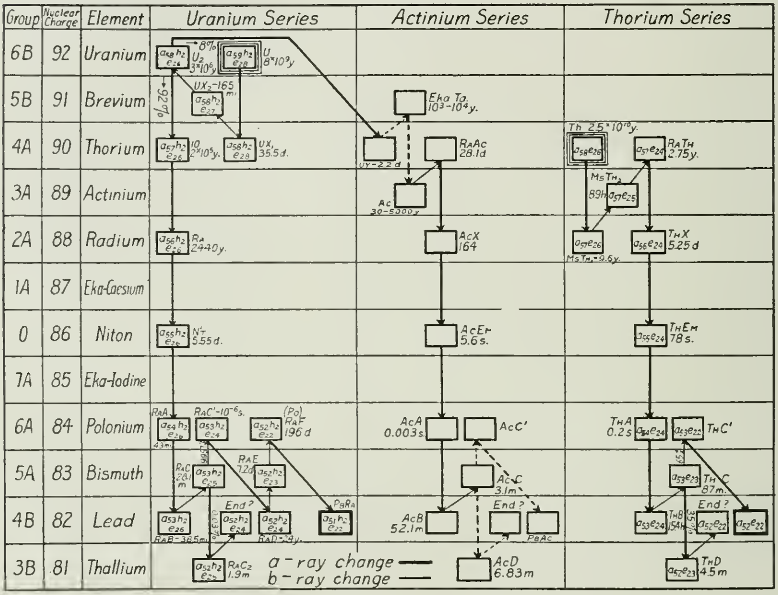
> During the period in which Davy and Gray-Lussac were carrying on their brilliant work, and before the star of Berzelius had attained to its full lustre, a literary chemical event occurred which made a profound impression upon nearly all the chemists of that day, *viz.*, the advancement of Prout's hypothesis. This was one of the factors which materially depreciated the atomic doctrine in the eyes of many eminent investigators. On account of its influence upon the further development of the atomic theory this hypothesis must be discussed here, although it but seldom happens that an idea from which important theoretical conceptions sprang, originated in so faulty a manner as it did.

2. THE WHOLE NUMBER RULE: HYDROGEN THE ONLY TRUE ELEMENT.

That the atomic weights are not at all whole numbers when the atomic weight of hydrogen is taken as unity, is shown very plainly in column 2 of Table II. *Thus Prout's hypothesis in its numerical form is not at all true.*

However, the data presented in columns 5 and 6 of the table indicate that the atomic weights of the first twenty-seven elements, with the omission of hydrogen, are, with very few exceptions, very close to the whole numbers, if oxygen as 16 is taken as the basis for the atomic weights. These facts led Harkins and Wilson in 1915 to the first statement of the *Whole Number Rule.* This may be expressed as follows: First, *The atomic weight of any pure* *atomic species is very close to a whole number on the basis of 16 as the atomic weight of oxygen* (or of 12 as the atomic weight of carbon, etc.). Second, *The atomic weight may be expected to be even closer to a whole number when it is divisible by 4 than when it is not so divisible.* The simplest explanation of the first and more fundamental part of this rule is that *all atoms other than hydrogen are intra-atomic compounds of hydrogen.* On this basis the whole number rule may be restated in a very simple form. The atomic weight of free hydrogen itself is 1.0078, but the average atomic weight of hydrogen which is combined in any other atom is in general equal to 1.000 (± 0.001).

FIG. 1.



Thus hydrogen itself, or hydrogen in any of its loose combinations known as molecular compounds, has an atomic weight equal to 1.0078, but in general when it enters into the extremely stable combination with itself found in any complex atom, it loses mass to the extent of $\frac{77}{001}$ per cent. Thus this loss of mass may be considered as the expense of the combination and may be indicated technically as the "packing effect." The origin of this packing effect will be discussed later in the section on "Mutual Electromagnetic Mass."

The second part of the rule, that the atomic weights are probably closer to whole numbers when they are divisible by 4, is a condition which may need to be imposed upon the first fundamental clause. According to the writer's theory atoms whose atomic weights are divisible by 4 have nuclei which are in general built up wholly from alpha particles which are known to be the nuclei of helium atoms. Now if the aggregation of these alpha particles does not materially influence the packing effect, it is a necessary result, provided there is no appreciable packing effect between the alpha particles, that the atomic weights of all such atoms should be divisible by the atomic weight of the helium atom, which would be one-fourth of the atomic weight of the oxygen atom, or exactly 4. On this basis all of the atoms of this class would have whole numbers for their atomic weights. Any hydrogen atoms which are not bound into helium atoms might exhibit some other value of the packing effect. If we assume that the lithium atom consists of one helium atom and three hydrogen atoms, and that the latter retain the masses they possess when free, then the atomic weight of this isotope of lithium would be 7.023 and on a similar basis the atomic weight of nitrogen would be 14.016. The experimentally determined atomic weight of nitrogen is 14.008, and it is a problem of prime importance to determine if the 0.008 is due to error, to the presence of a heavier isotope, or to a smaller packing effect than exists in atoms which are aggregates of helium atoms alone.

The general theory indicates that even for those atoms which are intra-atomic compounds alone, the whole number rule cannot be expected to be entirely exact. The possible deviations will be discussed in connection with a consideration of the energy emitted during the disintegration of radioactive atoms.

While the validity of the whole number rule as thus developed in 1915 is now universally recognized, it may be of historical interest to present a part of the discussion on this subject as published at that time, since it will help to show in what way the chemical atomic weights were interpreted.

In discussing the deviation of the atomic weights on the basis of hydrogen as 1, from a whole number, Harkins and Wilson stated:

TABLE II.

Deviations of the Atomic Weights from Whole Numbers.

	At. wt. H = 1.	Diff. from whole number.	Per cent. variation or the packing effect.	Possible per cent. variation.	At. wt. O = 16.	Diff. from whole number.	Per cent. variation from whole no.	Prob. error in at. wts.
H*....	1.000	....	....	....	1.0078	+0.0078	0.78	0.0002
He†...	3.97	−0.03	−0.77	12.5	4.00	0.00	0.00	0.01
Li.....	6.89	−0.11	−1.62	7.1	6.94	−0.06	−0.86	0.01
Be....	8.93	(+0.03)	....	5.5	9.0	+0.0	0.00	0.05
B.....	10.91	−0.09	−0.77	4.5	11.0	0.00	0.00	0.05
C‡....	11.91	−0.09	−0.77	4.2	12.00	0.00	0.00	0.005
N.....	13.90	−0.10	−0.70	3.6	14.01	+0.01	+0.07	0.005
O.....	15.88	−0.12	−0.77	3.1	16.00	0.00	0.00	0.00
F.....	18.85	−0.15	−0.77	2.6	19.00	0.0	0.0	0.05
Ne‡...	19.85	....	....	....	20.0	....	....	....
Na§...	22.82	−0.18	−0.77	2.2	23.00	0.00	0.00	0.01
Mg...	24.13	+0.13	+0.55	2.15	24.32	+0.32	+1.33	0.03
Al....	26.89	−0.11	−0.77	1.85	27.0	0.00	0.00	0.0
Si.....	28.08	+0.08	+0.31	1.78	28.1	+0.10	+1.07	0.1
P.....	30.78	−0.22	−0.71	1.61	31.04	+0.04	+0.12	0.01
S‡....	31.82	−0.18	−0.56	1.56	32.07	+0.07	+0.22	0.01
Cl....	35.19	+0.19	+0.54	1.43	35.46	+0.46	+1.31	0.01
Ar....	39.57	−0.43	−1.07	1.25	39.88	−0.12	−0.30	0.02
K.....	38.80	−0.20	−0.52	1.28	39.10	+0.10	+0.25	0.01
Ca....	39.76	−0.24	−0.60	1.25	40.07	+0.07	+0.17	0.03
Sc....	44.76	−0.24	−0.55	1.14	45.1	+0.10	+0.23	0.2
Ti....	47.73	−0.27	−0.57	1.04	48.1	+0.10	+0.21	0.1
V.....	50.61	−0.39	−0.77	0.98	51.0	0.0	0.0	0.1
Cr....	51.60	−0.40	−0.77	0.96	52.0	0.0	0.0	0.05
Mn...	54.50	−0.50	−0.90	0.90	54.93	−0.07	−0.13	0.05
Fe....	55.41	−0.59	−1.06	0.89	55.84	−0.16	−0.29	0.03
Co....	58.51	−0.49	−0.83	0.85	58.97	−0.03	−0.05	0.02

Per cent. variation of 21 elements (omitting Be, Mg, Si, Cl), or the packing effect.. = 0.77 %

Average deviation of the atomic weights, H = 1, from whole numbers = 0.21

Theoretical deviation of atomic weights from whole numbers on the basis that the deviations are entirely accidental................ = 0.25

Average deviation of the atomic weights, H = 1, for the eight elements from helium to fluorine.. = 0.095

Average deviation of the atomic weights, O = 16, when Mg, Si and Cl are omitted.. = 0.05

Average deviation of the atomic weights, O = 16, for the eight elements from helium to fluorine.. = 0.009

*W. A. Noyes (" A Text-book of Chemistry," p. 72) states that the atomic weight used for hydrogen, 1.0078, is probably not in error by so much as 1 part in 5000.

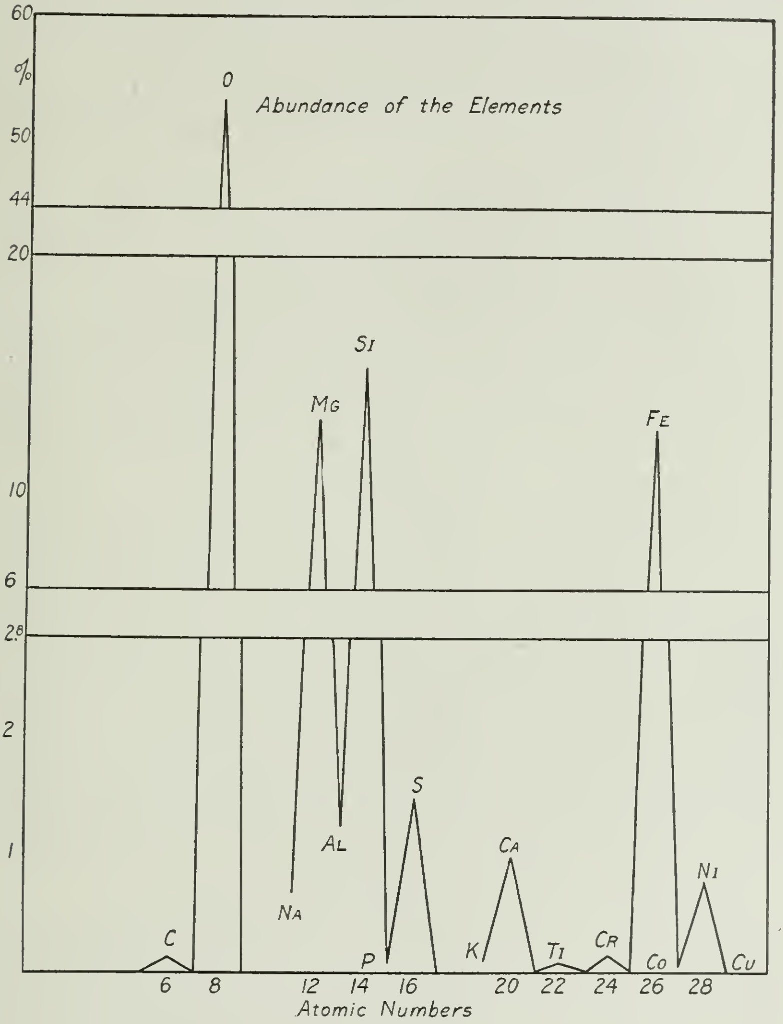
†Heuse (*Verh. duet. physik. Ges.*, 15, 518 (1913)) obtained the value 4.002 as the result of 7 experiments.

‡Leduc (*Compt. rend.*, 158, 864 (1914)) gives the atomic weight of neon as 20.15 when hydrogen is taken as 1.0075. Leduc's value is not used, on account of the discovery of the complexity of neon as described in the text of the paper.

§Richards and Hoover (J. Am. Chem. Soc. 37, 95 (1915)) determined the atomic weights of carbon as 12.005 and of sodium as 22.995, and in Vol. 37, p. 108, they give the atomic weight 06.of sulphur as 32.

Not only is the variation from a whole number a negative number, but in addition its numerical value is nearly constant, the average value for the twenty-one elements being 0.77 per cent., while the six elements from boron to sodium show values of 0.77, 0.77, 0.70, 0.77, 0.77, and 0.77 per cent. The deviation is therefore not a periodic, *but a constant one*. If, then, a modification of Prout's hypothesis that the elements are built up of hydrogen atoms as units is to be taken as a working basis, it becomes important to find a cause for the decrease in weight which would result from the formation of a complex

FIG. 2.



atom from a number of hydrogen atoms. The regularity in the effect suggests that, in general, this decrease in weight is probably due to some common cause, though the exceptional cases of magnesium, silicon, and chlorine, show that there is certainly some other complicating factor. The discovery of the reason for the deviation of the same kind in the case of neon, where it is due to its admixture with an isotope of higher atomic weight, suggests that it may not be impossible to find explanations for these three other exceptions.

In order to have a term for the percentage decrease in weight, it may be well to call this the packing effect, or percentage variation from the commonly assumed law of summation, that the mass of the atom is equal to the sum of the masses of its parts.

It has formerly seemed difficult to explain why the atomic weights referred to that of oxygen as 16 are so much closer to whole numbers than those referred to that of hydrogen as one, but the explanation is a very simple one when the facts of the case are considered. *The closeness of the atomic weights on the oxygen basis to whole numbers, is indeed extremely remarkable.* Thus for the eight elements from helium to sodium the average deviation is only 0.02 unit, which is less than the average probable error in the atomic weight determinations. When twenty-one elements are taken from the table, omitting the exceptional cases of magnesium, silicon, and chlorine, the deviation averages only 0.05 unit, while if these are included, this is increased only to 0.09 unit. These results have been calculated without taking the sign into account. If the sign is considered the average deviation is reduced to 0.01 unit for the twenty-one elements. The probability that such values could be obtained by accident, is so slight as to be unworthy of consideration. If an oxygen atom is a structure built up from sixteen hydrogen atoms, then the weight according to the law of summation should be sixteen times 1.0078, or 16.125. The difference between 16.125 and 16.00 is the value of the packing effect, and if this effect were the same for all of the elements, except hydrogen, then the choice of a whole number at the atomic weight of any one of them, would, of necessity, cause all of the other atomic weights to be whole numbers. Though this is not quite true, it is seen that the packing effect for oxygen is 0.77 per cent., which is the average of the packing effects for the other twenty-one elements considered. Therefore, those elements which have packing effects equal to that of oxygen will have whole numbers for their atomic weights, and since the other elements show nearly the same percentage effect. their atomic weights must also lie close to whole numbers.

Earlier in the paper it has been shown that the fact that the atomic weights on the oxygen basis are much closer to the whole numbers than those on the hydrogen basis, is explained by what has been called the packing effect, or the change of mass involved in the formation of heavier atoms from hydrogen. The average of the packing effects for the elements considered is 0.77 per cent. This is also the value of this effect for oxygen, which happens to have been chosen as the fundamental element in the determination of atomic weights. If the number representing atomic weight of hydrogen, 1.0078, is decreased by this percentage amount, it becomes 1.0000, *which is the fundamental unit in atomic weight determinations.* The atomic weights of the twenty-five fundamental elements listed in Table II are found, on the whole, to be very nearly products of this unit by a whole number. While the numerical unit of measurement does not change, the actual unit of mass, the mass of the hydrogen nucleus varies slightly from atom to atom, and this variation may cause a slight deviation of the atomic weights from whole numbers.

The opposite of the system here proposed would be, to suppose that the values of the atomic weights are wholly the result of accident. On this basis the probability that the atomic weights fall as close to whole numbers as they do, may be calculated. In such calculations oxygen is omitted, since its atomic weight is fixed as a whole number, and hydrogen is not used, since its atom contains only one hydrogen nucleus.

The first calculation made was that of the probability that *each* of the atomic weights should be as close as it is to a whole number. The data used are those of Table II. The chance that the atomic weight of nitrogen should entirely, by accident, deviate from a whole number by only 0.01 of a unit was determined by dividing the unit into the 200 divisions corresponding to the assumed accuracy (Landolt-Börnstein-Meyerhoffer, Tabellen) of 0.005. The greatest possible deviation would then be 100 divisions, while the actual deviation of 0.01 unit corresponds to two divisions. The probability is then one-fiftieth. The chance that any number of independent events should all happen is the product if the separate probabilities of their each happening. The probability calculated in this way is 2×10^{-23}, or

$$\frac{2}{10{,}000 \text{ billion billion}},$$

which indicates that there is practically no chance that the atomic weights are entirely the result of accident.

Another probability, which seems to be of more value in connection with the present problem, is that the *sum* of the deviations shall not exceed the sum actually found. This is of the form known as De Moivre's problem, and the method was used by Laplace[3] in calculating the probability that the sum of the inclinations of the orbits of the ten planets to the ecliptic is not greater than the value found at that time, 0.914187 of a right angle. The result obtained was 1.1×10^{-7}. The problem is stated in the following way: An urn contains $n + 1$ balls marked, respectively, 0, 1, 2, 3, . . . n; a ball is drawn and replaced: required the probability that after i drawings the sum of the numbers drawn will be s. This probability is the coefficient of x^s in the expansion of

$$\frac{1}{(n+1)^i}\,(1 - x^{n+1})^i(1 - x)^{-i},$$

or the probability P is

$$P = \frac{1}{(n+1)^i}\left\{\frac{\underline{|i+s-1}}{\underline{|i-1}\;\underline{|s}} - \frac{i}{1}\,\frac{\underline{|i-1+s-n-1}}{\underline{|i-1}\;\underline{|s-n-1}} + \frac{i(i-1)}{1.2}\,\frac{\underline{|i-1+s-2n-2}}{\underline{|i-1}\;\underline{|s-2n-2}}\;\cdots\right\}.$$

In the case of the atomic weights P gives the probability that the sum of the deviations from whole numbers shall equal s, which is not what is desired. The result wanted is the probability that the sum of the errors shall be equal to or less than s, or the summation of the Ps from 0 to s. Now

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[3] Laplace: "Oeuvres VII, Theorie Analytique des Probabilites," pp. 257–62.

$$\sum_{s=o}^{s=s} \frac{\underline{|i+s-1}}{\underline{|i-1}\ \underline{s|}} = \frac{\underline{|i+s}}{\underline{|i}\ \underline{|s}}.$$

So the desired probability, P′ is:

$$P' = \sum_{s=o}^{s=s} P = \frac{1}{(n+1)^i} \left\{ \frac{\underline{|i+s}}{\underline{|i}\ \underline{|s}} - \frac{i}{1} \frac{\underline{|i+s-n-1}}{\underline{|i}\ \underline{|s-n-1}} + \right.$$

$$\left. \frac{i(i-1)}{1.2} \frac{\underline{|i+s-2n-2}}{\underline{|e}\ \underline{|s-2n-2}} - \frac{i(i-1)(i-2)}{1.2.3} \frac{\underline{|i+s-3n-3}}{\underline{|i}\ \underline{|s-2n-3}} \cdots \right\}.$$

In solving this problem all of the first twenty-seven elements have been used with the exception of hydrogen and oxygen, and these *should* be omitted for the reasons given above. The errors in the determined values have been taken as they are given in Table II. The atomic weights used in the calculation are as follows:

He	4.002	Mg	24.32	Ca	40.07
Li	6.94	Al	27.1	Sc	44.1
Be	9.1	Si	28.3	Ti	48.1
B	11.0	P	31.02	V	51.0
C	12.005	S	32.06	Cr	52.0
N	14.01	Cl	35.46	Mn	54.93
F	19.00	A	39.88	Fe	55.84
Ne	20.15	K	39.10	Co	58.97
Na	22.995				

The average probable error as determined from Table I is 0.043 unit, which is equivalent to about twenty-four divisions for one unit, or twelve divisions for half a unit, which is the maximum possible deviation from a whole number. Since n is 12, $n + 1$ is taken as 13. The sum of the deviations from whole numbers is 2.342, which is equal to fifty-six of the divisions determined above, or $s = 56$. The number of elements, i, is 26. The probability calculated on this basis is 6.56×10^{-8}, or approximately

$$\frac{1 \quad *}{15{,}000{,}000}.$$

It has been assumed in this paper that the cause of the deviations of neon, magnesium, silicon, and chlorine, which are exceptional in giving positive deviations from the atomic weights on the hydrogen basis, must be different

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*Since this was calculated the atomic weights have been changed by new determinations so that they are closer to whole numbers by the following amounts: Be, 0.07 unit; Al, 0.07 unit; Si, 0.2 unit. Thus this probability is now far smaller than

$$\frac{1}{15{,}000{,}000}.$$

from that which gives the deviations of the other elements. The cause of the deviation of neon has been explained, but for the others it is unknown. In the calculations of the probabilities given above these elements have been included. It may be of interest to note that if these elements had been excluded the probability for the twenty-one remaining elements would have been found to be about

$$\frac{1}{7 \text{ billion}}.$$

It is an interesting coincidence that the probability above found for the twenty-seven lighter elements is about 1×10^{-7}, while the probability determined by Laplace that the sum of the inclinations of the ten planets then known, to the ecliptic, should not be greater than the sum of the measured values, is almost the same, or 1.123×10^{-7}. In the second paper of this series it will be shown that the atomic weights not only approximate whole numbers, but that these whole numbers are in addition *certain* numbers which are determined by a special system, and which may be given accurately by an equation of the form

$$W = 2(n + n') + \tfrac{1}{2} + [(-1)^{n-1} \times \tfrac{1}{2}].$$

The probability that the atomic weights should come so close to these *special* whole numbers is much less than that calculated above, so that the words of Laplace may be applied to the system presented here, as well as to the one he himself gives. *That the atoms are built up of units of weight very close to one,* and that therefore this modified form of Prout's hypothesis holds, "est indiquee avec une probabilite bien superieure a celle du plus grand nombre des faits historiques sur lesquels on ne se permet aucun doute."

The accepted atomic weights on the oxygen basis as now used are closer to whole numbers than those given by Ostwald in 1890.[4] Ostwald's numbers are all larger than the corresponding whole numbers, so the deviations were all positive. On the other hand, the present values show both positive and negative deviations. The fact that the small change of 0.77 per cent. from the oxygen to the hydrogen basis eliminates practically all of the tendency of the atomic weights to be near whole numbers, when as many as twenty-seven elements are considered as in Table II, shows that the atomic weight of oxygen cannot be taken as very different from 16.00 without obscuring this relationship. Thus it has been shown that the probability that the atomic weights on the oxygen basis would come entirely by accident as close to whole numbers as they do, is 6.56×10^{-8}, or about

$$\frac{1}{15{,}000{,}000}.$$

A change of only 0.77 per cent. from the oxygen basis causes an enormous increase in the probability that the atomic weights obtained in this way could be as close to whole numbers as they are, entirely by accident. Thus the chance that the sum of the deviations should come out as equal to, or less than, the sum actually found, is 0.105, or

$$\frac{1}{10}.$$

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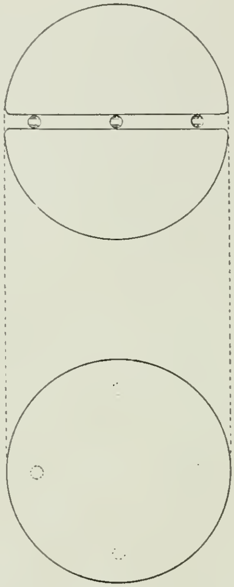
[4] *Allgemeine Chemie,* I, p. 126 (1890).

As has been seen, there are twenty-seven atomic weights distributed over fifty-nine units of atomic weight. The greatest common divisor of the whole numbers corresponding to the atomic weights is one. *The atomic weights are therefore such that numerically they seem to be built up from a unit of a mass of one, and the probability results seem to show that this unit of mass must be very close to 1.000, expressed to three decimal places.*

FIG. 3.



Model of the alpha particle or nucleus of the helium atom.
The two large deformed spheres represent negative, and the four small spheres positive, electrons.

3. THE NEGATIVE ELECTRON AND THE POSITIVE ELECTRON.

The phenomena concerned with the displacement of negative electrons (negative charges of electricity) are so universal that they have been recognized for thousands of years. Thus a silk cloth rubs off negative electrons from a glass rod, while when fur and a piece of sulphur or rubber are rubbed together these electrons pass from the fur to the other object. Negative electrons escape in considerable numbers from hot wires, they are supposed to be the carriers of electricity in wires, and are driven out of various materials by the action of radiation.

Negative electrons were first discovered in the electrical charges in vacuum tubes. As early as the year 1859, Plücker showed that the rays produced in such tubes may be deflected by a magnet, and about ten years later Hittorf found that they travel in a straight line and will not follow a bend in the tube. Varley first considered these rays to consist of electrified matter from the cathode, while Crookes believed them to be a fourth state of matter. In 1895 Perrin proved directly that they carry negative electricity, and the discovery of the electron as a particle or corpuscle was made two years later by J. J. Thomson and by Wiechert.

The charge carried by the negative electron has been found to be 4.77×10^{-10} electrostatic units, while its mass is 1835 times less than that of the lightest atom, that of hydrogen.

Nearly 100 years ago Faraday showed by what is known as the ice-pail experiment that, when electricity is produced, the positive and negative electricity are equal in magnitude, and appear simultaneously. While the smallest mass associated with the negative electron is much smaller than that of the hydrogen atom, the smallest positively charged particle has been found to have practically the mass of the hydrogen atom (1.66×10^{-24} grams). Instead of giving the mass of the hydrogen atom in grams it is customary to designate it as 1.0078. If it is assumed that the hydrogen atom consists of a positive ion and a negative electron, the mass of the former would be 1.0023, while that of the latter would be 0.0055.

Since the hydrogen ion mentioned in the previous paragraph has in no case been split up into anything which possesses a smaller mass, and since it is the lightest particle ever found to carry a positive charge, it may be properly designated as the *positive electron,* especially since atomic weights indicate strongly that the heavier atoms are built up of hydrogen.

4. THE PRINCIPLE OF ELECTRICAL NEUTRALITY.

It has been found by experiment that material bodies at ordinary temperatures are not in general set in motion by being placed in a uniform electrical field, or they are in the state which is commonly designated as uncharged. Since, however, electrically charged particles can be obtained from all such bodies, it has been concluded that the " uncharged " condition does not indicate that they do not contain electric charges, but rather that the positive and negative electricity are present in each uncharged body in equivalent amounts, a condition which is designated by the term electrically neutral. This idea of electrical neutrality is in accord with the Faraday ice-pail experiment mentioned in an earlier paragraph, and has been extensively used in the study of aqueous solutions of electrolytes. Thus in a salt solution it is considered that the number of equivalents of negative ions present in any solution is equal to the number of equivalents of positive ions.

The idea of electrical neutrality has been utilized in all of the prevalent theories of the structure of the atom. Thus the number of elementary positive charges in any complete atom is supposed to be equal to the number of elementary negative charges. If it is supposed that these elementary charges are due to the presence of electrons, this would mean that *the number of positive electrons in any atom is equal to the number of negative electrons.* Any atom which is not electrically neutral is designated as an ion, and may be charged either with a net negative or a net negative charge. In an ion the number of positive electrons is in no case equal to the number of negative electrons.

One positive plus one negative electron may be designated as an *electron pair,* which may be indicated by the symbol *p,e.* Here *p* represents a positive, and *e* a negative, electron, and the comma is used when it is not assumed that there is a definite union between the two. The symbol *pe* will be used to represent a neutron, or a positive and a negative electron in an extremely close combination.

While the atomic weight of the electron pair which constitutes the hydrogen atom is 1.0078, it has been stated that the mean atomic weight of an *electron pair* in any other atom is very close to 1.000. *Thus the atomic weight of any species of atoms gives the number of electron pairs in each of its atoms,* so the atomic weight of oxygen, 16, indicates that the oxygen atom consists of 16 electron pairs, that is, of 16 positive and 16 negative electrons, and its formula is $p_{16}e_{16}$. Calcium [5] with an atomic weight of 40 is $p_{40}e_{40}$, while the principal atomic species of the element argon has also an atomic weight of 40, and is also $p_{40}e_{40}$. *Thus calcium and this argon are isomeric atomic species.* The term isomeric indicates that they are represented by the same formula, and thus contain the same number of negative and also the same number of positive electrons. That such atoms should be designated as isomeric was proposed by the writer several years ago. The term is certainly preferable to *isobaric,* which is sometimes used, since the latter term indicates only that the atomic weights are the same, *which may not be strictly true,* while the term isomeric expresses not only that the atomic weights are very close to the same whole number but also the identity with respect to the number of each type of electron present, as expressed above. The nuclei of *isomeric* atoms are nearly *isobaric* and are not isomeric.

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[5] This refers to the most abundant isotopes.

5. THE NUCLEAR ATOM.

The prevalent idea of the atom is that it consists of a minute nucleus surrounded by a system of negative electrons. This nucleus is supposed to contain practically all of the mass, and also all of the positive electricity of the atom. An atom of this type is sometimes designated as a solar system, in which the nucleus takes the place of the sun, and the planets are represented by negative electrons, which may be called planetary electrons. These electrons and the nucleus are supposed to be at somewhat the same relative distances in comparison with their dimensions as the planets and the sun.

This type of atom was first suggested in 1903 by Nagoaka,[6] but the evidence for it is due largely to Rutherford.[7] According to the earlier suggestion of Lord Kelvin [8] and of J. J. Thomson, the positive electricity in an atom is distributed in a diffuse sphere or disc, but Rutherford discovered certain facts, described in the following paragraph, which did not seem to be in harmony with this idea.

When radium and certain other radioactive substances disintegrate, they emit alpha particles. These alpha particles carry two elementary positive charges of electricity, their mass is 4 or that of the helium atom, and they travel at high speeds, as great as 20,000 miles per second. Now Rutherford and his collaborators —Geiger, Marsden, and Darwin—found that when these alpha particles are shot through various substances, such as hydrogen or gold, the alpha particles are occasionally deflected with extreme sharpness, and even turned back almost directly in their path. In general the path is that of one limb of an hyperbola, and by considering the simple mathematical relations of such a path they were able to show that the positive electricity in an atom is concentrated in a small nucleus and to make an approximate calculation of the diameter of this nucleus. It was found that the maximum diameter of the nucleus of a gold atom is 6.8×10^{-12} cm., while that for the hydrogen nucleus is 1.7×10^{-13} cm. Since an atom is of the order of 2×10^{-8} cm. in diameter, this indicates that the atom has a diameter from 2000 to 100,000 times that of the nucleus, or its volume is from a few million to several billion times as great. The diameter of the negative electron is usually given as 2.0×10^{-13} cm., so the nucleus of an atom seems to be of somewhat the same size as the electron. It is not unlikely that the hydrogen nucleus may be smaller than the electron, but it seems probable that all other atom nuclei are somewhat larger. Evidence will be presented later, which seems to indicate that while the hydrogen nucleus does not contain a negative electron (being itself presumably the positive electron) all other nuclei of stable atoms contain two or more negative electrons.

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[6] Nagoaka: *Phil. Mag.*, **7**, 445 (1904).

[7] Rutherford: *Ibid.*, **21**, 669 (1911), and later papers.

[8] Kelvin: *Phil. Mag.*, **3**, 257 (1902).

6. EVIDENCE FOR THE PRESENCE OF NEGATIVE ELECTRONS IN ATOM NUCLEI.

Since the nucleus of an atom may be defined as that part in which the positive charge resides, it would seem evident that the positively charged alpha particles, which are emitted at high speed by radioactive atoms, must come from the nucleus. Certain radioactive substances, instead of emitting alpha particles, eject beta particles or negative electrons at speeds which closely approach the velocity of light, and rise as high as 180,000 miles per second. On account of the considerable energy which they possess Rutherford concluded that these negative electrons cannot come from the non-nuclear system of electrons, but must be thrown out by the nucleus itself. Even better evidence than this that both the alpha and beta particles are ejected from the nucleus is given by the change which occurs in the chemical and physical properties of the elements, and the change of the atomic number which accompanies such phenomena. These will be described later in detail. Since the evidence given by the radioactive elements relates only to the heaviest elements, it may be seen that it might be possible that light nuclei do not contain negative electrons. Thus Nicholsen considered that the alpha particle consists of two hydrogen nuclei, each with a unit positive charge, and that the mass 4 of the helium nucleus is due to a squaring of the mass due to the proximity of like charges. It will be found, however, that it is much simpler to assume that the alpha particle (helium nucleus) consists of 4 positive and 2 negative electrons.

7. EXPLANATION OF THE PACKING EFFECT AS DUE TO ELECTROMAGNETIC MASS.

According to the electromagnetic theory of Lorentz the mass of an electron increases with its velocity, so at least a part of its mass appears concomitantly with the appearance of kinetic energy. In the special relativity theory mass and energy are identical, but are expressed in different units. The idea of the equivalence of mass and energy may be used in explaining the packing effect.

If a stone falls to the earth its potential energy, due to its position, disappears, and just this amount of energy reappears in other forms, mostly as heat, when the stone strikes the ground. When a positive and a negative electron are relatively far apart as in a hydrogen atom, the mass of the electron pair is 1.0078. If, however, due to their mutual attraction the positive and the negative electron were to fall closer together, a part of the original potential energy, due to their attraction at a distance, would disappear, and this amount of energy would be given off in some way, presumably as a form of radiation. The energy given off would be equal to 0.0078 units of mass, so the resulting neutron (*pe*) would have a mass of 1.000. While there is at present no indication that such a simple system will do this, it seems probable that four positive electrons will under some circumstances unite with two negative electrons to form an alpha particle (helium nucleus), and this would then pick up two additional non-nuclear electrons to form a neutral helium atom. The difference in mass between four hydrogen atoms and one helium atom, amounts to a decrease of 0.77 per cent., or the magnitude of the packing effect.

While the writer was working in the endeavor to show definitely that the packing effect could be due to electromagnetic effects, Rutherford[9] made the suggestion that there *might be* such an effect in the formation of helium, as is indicated by the two following paragraphs:

> The exceedingly small dimensions found for the hydrogen nucleus add weight to the suggestion that the hydrogen nucleus is the positive electron, and that its mass is entirely electromagnetic in its origin.

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[9] *Phil. Mag.*, 27, 494–5 (1914).

> For the dimensions of the positive and negative electrons considered, the packing must be very close in order to produce an appreciable alteration in the mass due to this cause. This may, for example, be the explanation for the fact that the helium atom has not quite four times the mass of the hydrogen atom.

Comstock had previously [10] suggested that the absence of exact relations among the atomic weights might be due to differences in the velocities of the electrons, but he explained only the deviations from whole numbers on the oxygen basis in this way. These deviations do not need to be explained since they are plainly due to the existence of isotopes, and the deviation between hydrogen and helium is too great to be explained in this way. Nevertheless, Comstock's paper deserves attention as a beginning in the application of the ideas of the electromagnetic theory to this field.

Harkins and Wilson made certain preliminary calculations which seemed to indicate that when a positive electron approaches a negative electron the loss of mass might amount to as much as 0.77 per cent., which is the value of the experimental packing effect. The actual solution of the problem was carried out for them by Prof. A. C. Lunn, of the Department of Mathematics, University of Chicago, and will be given in a later section. Only an approximate solution was attempted, since it seems likely that the inverse square law does not hold at such minute distances as those between the positive and negative electrons in a complex nucleus. According to Professor Lunn's calculation, based on the simplifying assumption of point charges, the change of mass, or packing effect, due to the overlapping of the electromagnetic fields of two electrons is

$$\Delta = m \pm \frac{e^2}{2\pi c^2 d} \qquad (1)$$

in Heaviside units. In this equation Δm is the change of mass, e is the charge on the electron, c the velocity of light, and d is the distance between the centres of the electrons. The ± sign indicates that the mass increases if the two electrons have like charges, but decreases when they are oppositely charged. Since it may be expected that in a complex system the electrons will arrange themselves so that electrons of unlike charge lie closest together,

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[10] *J. Amer. Chem. Soc.*, 30, 683 (1908).

the effect to be expected is a decrease of mass, as in accord with the experimental data.

The longitudinal mass of an electron is

$$m = \frac{e^2}{6\pi c^2 R} \tag{2}$$

where R is the radius of the electron.

By division of (1) by (2)

$$\frac{\Delta m}{m} = \frac{3R}{d}. \tag{3}$$

Since only the positive electron has an appreciable mass, R may be taken as the radius of the positive electron. Equation 3 then states that for a change of mass of 1 per cent., $\frac{\Delta m}{m} = 0.01$, or $\frac{3R}{d} = 0.01$, so $d = 300R$, or the distance between the centres of the electrons should be 300 times the radius of the positive electron. For a packing effect of 0.77 per cent. it is evident that the distance between centres should be approximately $400R$. This would make it seem plausible that the packing effect of 0.77 per cent. is due to an electromagnetic mass effect.

In conversation with the writer, Silberstein has claimed that when the distribution of charges in the electrons is taken account of, the change of electromagnetic mass is too small to account for the considerable magnitude of the packing effect, since the latter is so great as to make it necessary that the positive electron shall lie partly inside the negative one. According to equation 2 given above, which may not be entirely correct, the positive electron should have a radius only 1/1835 that of the negative electron, since the radius is inversely proportional to the mass. It seems to the writer the probability that the packing effect is due to electromagnetic mass effects is not decreased by a consideration of Doctor Silberstein's equations, since:

1. The equations in any event are only approximate.
2. The equations are based on the inverse square law, which is believed by the writer to be very likely to fail at such minute distances. Rutherford's experiments seem to indicate that this law fails very close to the nucleus.
3. The positive electrons may lie in indentations in the negative electrons.
4. We have no evidence that the positive electrons may not lie partly or wholly within the negative electrons.

5. Deformations of either the positive or the negative electrons would affect the packing effect. If, for example, it is assumed that the attraction between the positive and negative electrons not only draws them close together, but that it also causes the charges of the two electrons of opposite sign to become concentrated largely at their region of contact, it is easily seen that the resulting decrease of electromagnetic mass might be very much greater than the packing effect actually found (0.77 per cent.). As has already been stated, it is obvious that the important factor is the loss of mass of the positive electron, since the mass of the negative electron is too small to be greatly decreased.

While nothing has been said in the preceding paragraphs of the effect of the velocities of the electrons in producing slight variations of the packing effect, it is not improbable that such effects may exist to an extent which would be detectable by very delicate measurements, but it is evident that the loss of mass of 0.77 per cent. cannot be due to such a cause, since in the hydrogen atom neither the positive nor the negative electron is moving with a sufficient velocity to give an appreciable mass due to this cause. It is evident that any mass change of this type must be represented by a higher mass in the complex atoms.

8. THE ATOMIC NUMBER GIVES THE CHARGE ON THE NUCLEUS AND THE NUMBER OF NUCLEAR ELECTRONS.

In 1911 Barkla,[11] from his work on the passage of X-rays through matter suggested that the positive charge on the nucleus of the atom is about half the atomic weight. Now the ordinal number of an element in the periodic system, as first given by Rydberg in 1896, is approximately half the atomic weight, so this suggested to van den Broek that the ordinal number of the element gives the number of elementary positive charges on the nuclei of its atoms. Van den Broek [12] designated this as the atomic number, which is the term now in use, though it is much less exact than that used by Rydberg.

The suggestion of van den Broek was strongly supported by the remarkable work of Moseley on the X-ray spectra of the elements. Using a method first suggested by Laue[13] and Bragg,[14] Moseley[15] and Darwin developed an experimental method for determining the X-ray spectra of the elements by reflection from a crystal surface. When an element is used as an anti-cathode in an X-ray tube it emits characteristic radiations of a frequency roughly 1000 times that of ordinary light. Each element was found by Moseley to be characterized by two different classes of radiation, the K series, with the highest frequency, and the L series, with a lower frequency. Other series of still lower frequency have since been found. The K series showed in Moseley's photographs as consisting of two lines, an alpha and a beta line, and these were used by him for most of his calculations. More lines were found in the L series.

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[11] Barkla: *Phil. Mag.*, **21**, 648 (1911).

[12] van den Broek: *Physik. Z.*, **14**, 33 (1913).

The remarkable feature of Moseley's photographs is that they show that the frequency of the K series lines constantly increases in a very regular way as the atomic number increases.

He found the frequency (v) to be a linear function of the square of the atomic number (M), sometimes called the Moseley number, according to the following simple equation:

$$v = K(M-1)^2$$

It is seen that the frequency of the radiation increases as the atomic number increases. Now if the atomic number represents the positive charge on the nucleus, this may be explained very simply. According to the theory of Bohr ordinary light is due to the falling of an electron from an outer orbit in an atom to one slightly closer to the nucleus. In the same way the K series of X-rays may be explained as due to the falling of an electron into the orbit closest to the nucleus from an orbit farther out. The frequency of the light emitted is supposed to be proportional to the energy of the fall. In comparable falls, that is between orbits of the same number in different atoms, as, for example, a fall from orbit 2 to orbit 1, the energy of the drop should increase with the magnitude of the attractive force between the electron and the nucleus, that is, with the charge of the nucleus. While the above description of Bohr's idea is too brief to be accurate, it may give a slight idea as to the meaning of Moseley's work. Either Bohr's papers or Sommerfeld's "Atombau" should be consulted for a more accurate description of the theory.

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[13] Laue: *Ann. Physik.*, **41**, 989 (1913).

[14] W. Bragg and L. Bragg: *Proc. Roy. Soc.*, **88A**, 428 (1913), **89A**, 246 (1914).

[15] Moseley: *Phil. Mag.*, **26**, 1024 (1913); **27**, 703 (1914).

Since the atom is supposed to be electrically neutral, the number of planetary negative electrons should be equal to the atomic number (M).

9. RADIOACTIVITY: THE SPONTANEOUS DISINTEGRATION OF ATOMS.

Early in 1896 Becquerel became interested in the new penetrating X-rays just discovered by Röntgen, and especially in the statement of H. Poincare that these rays are given off from the fluorescent spot on the glass produced by the cathode rays. It occurred to Becquerel to try an experiment to see if substances which are phosphorescent after their exposure to ordinary light give similar penetrating rays. Using a potassium-uranium double salt he was able to get such rays, which passed through paper and aluminium and affected a photographic plate. Later experiments showed, however, that the same effect was produced if the salt was not previously exposed to light. It was soon found that the phenomenon was not due at all to the fact that the salt was phosphorescent, but that it is a property of the element uranium.

About two years later Madame Curie discovered polonium and radium which exhibit the same phenomenon, but very highly intensified. Substances of this type are considered to be radioactive. In 1902 Rutherford classified the rays given off by such substances as follows:

1. Alpha rays, which are slightly but not greatly deviated by a magnet or by an electric field, and consist of particles which carry a double positive charge, and have the mass of a helium atom. It was afterward found that the alpha particle is the nucleus of the helium atom.

2. Beta rays, which consist of negative electrons, and are much more greatly deviated by either an electric or a magnetic field. They penetrate much greater thicknesses of material than alpha rays, that is, their range is much greater.

3. Gamma rays, which are not deviated by a magnet and carry no charge. These are very similar to extremely "hard" or penetrating X-rays, and they penetrate much greater thicknesses of material than either alpha or beta rays.

As has been stated in an earlier paragraph, both the alpha and beta particles are shot out at high speeds from the nucleus of the atom.

So far as is now known, a single atom never ejects more than a single alpha or a single beta particle at one time, and in no known case do both an alpha and a beta particle escape at once. In general, a certain species of atoms exhibits only one of the two classes of disintegration. Thus, for example, ionium, radium, radium emanation, radium A, radiothorium, and a number of others emit only alpha particles; while uranium X_I, uranium X_{II}, mesothorium I and II, radium C_2, radium E, etc., give off beta particles. A few species of atoms, such as radium C and thorium C, may disintegrate in either way, but a single atom disintegrates in only one of the two ways. For example, 99.97 per cent. of the atoms of radium C disintegrate by shooting out beta particles, and 0.03 per cent. by the emission of alpha particles.

There are three disintegration series—the uranium, the actinium, and the thorium series. The uranium series consists of uranium and about sixteen other atomic species, of atomic number from that of uranium (92) to that of thallium (81). All of these are formed by a series of one to fourteen disintegrations from the original ancestor, uranium. The ancestor in the thorium series is thorium, and for the actinium series is unknown. It is usually supposed that the actinium series is a branch from the uranium series. All three of the series begin to branch in the region of atomic number 82.

Figure 1 gives a diagrammatic representation of all three series, and is a modified form of a diagram given by Soddy. It will be seen that in an alpha change, represented by a long, heavy arrow pointing downward, the atomic number, and also the valence is decreased by two. In the ordinary form of the periodic system there is a change of two places to the left. In a beta change, represented by a short arrow, pointing diagonally upward, the atomic number and valence increase by one, and the element moves one place to the right in the ordinary periodic table. These relations to the periodic system were discovered by Fajans, Soddy, Russell, von Hevesy, and Fleck.

The formulæ given inside the rectangles in Fig. 1 are those which are valid for the nucleus of the atom, provided that each nucleus is built as completely as possible of alpha particles and electrons. In these formulæ ∞ represents an alpha particle, *h* a hydrogen nucleus or positive electron, and $\dot{e}$ a negative electron. Since it is assumed that each alpha particle consists of four positive and two negative electrons, it is apparent that there are a great many electrons present in the nuclei which are not indicated by the letter e. The electrons represented by this symbol may be styled "*cementing electrons*" while those in the alpha particles may be called "*binding electrons.*"

The figure gives also the average life of most of the atomic species. Thus the average life of an uranium atom is 8×10^9 years, while that of a thorium C′ atom is 10^{-11} seconds. Thorium has the greatest average life, 2.5×10^{10} years, of any of the radioactive substances listed. All three of the radioactive series are usually supposed to end in lead, since the radioactivity of lead of atomic weights 206 and 208 and of all lighter atoms, with the possible exception of potassium and rubidium, is so slight, that it has not been detected.

10. ISOTOPES.

About ten years ago a number of workers in the subject of radioactivity, among them Soddy and Fajans, began to realize that when they endeavored to fit the radioactive elements into the periodic system of Mendelejeff, there were more elements than there were places into which they could be fitted, as is illustrated by Fig. 1. However, it was found that in a number of cases a number of these elements, though their atomic weights were apparently different, appeared to have identical chemical properties, and aside from their density, appeared to have also identical physical properties. To designate a set of elements which were thus alike in properties, Soddy proposed to use the word isotopes (iso — tope = same place). While each isotope is essentially a different element, chemists and physicists were so used to considering all of the simple materials which behave alike chemically and have a certain atomic number, as constituting one element, that in spite of such differences in atomic weight all of the different atomic species of this type (isotopes) have come to be considered as a single element.

That isotopes usually have different atomic weights was apparent from the disintegration relations of the radioactive elements as exhibited in Fig. 1,[16] and was proved by direct atomic weight determinations made on the isotopes of lead by Soddy and by

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[16] Fig. 1 indicates the presence of seven isotopes of polonium, four of radium, and ten of lead.

Richards. The latter showed that the atomic volumes of these isotopes are the same within the limits of error of very careful experiments. The first and only chemical characteristic in which isotopes have been found to differ was discovered in an investigation suggested by the writer [17] and carried out by Aronberg, with the aid of suggestions by Professor Gale in regard to the spectroscopic technic. It was found that the wave-length of the line λ4058 in lead from radium (RaG) of atomic weight 206.33 is one ten-thousandth of 1 per cent. greater than that produced by ordinary lead of atomic weight 207.2. This result was afterward confirmed by Merton. It is apparent that the chemical and spectroscopic differences are small, but they may be of importance among the light elements where the atomic weight differences between isotopes rise to 16 per cent.*

II. THE HELIUM-HYDROGEN THEORY OF ATOMIC CONSTITUTION.

A definite helium-hydrogen system of atomic constitution was published by Harkins and Wilson [18] in the year 1915.† The first part of the present paper indicates that all of the atoms other than that of hydrogen itself, are intra-atomic compounds of hydrogen. The number of hydrogen atoms in any complex atom is given by the atomic weight of the latter on the basis of oxygen as 16. Thus the atomic weight 40 for calcium indicates that the ordinary calcium atom is H'_{40}, where the prime is used to indicate that the compound is intra-atomic and not molecular. However, since the hydrogen atom consists of one positive electron or proton (p) and one negative electron (e), this indicates that the general formula of the calcium atom is $p_{40}e_{40}$. However, in the formation of such an atom, while *all* of the protons enter the nucleus, only *half* of the electrons enter it, and the other half become planetary electrons, so the formula of the atom becomes $(p_{40}e_{20})\ e'_{20}$ where the parenthesis indicates the nucleus, and the planetary electrons are indicated by a prime.

It is of great interest that in the formation of light atoms just one-half of the negative electrons enter the nucleus (of the most abundant atomic species of the element), except that when the total number of negative electrons is odd and is not divisible by two the number of electrons entering the nucleus is the next whole number above one-half the number of protons. *Now this relation as it exists for the atoms of even atomic number is just that found in the helium atom, since helium is* $(p_4e_2)\ e'_2$, *that is just one-half of the negative electrons in the atom are found in the nucleus.*

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[17] Harkins and Aronberg: *Proc. Nat. Acad. Sci.*, 3, 710–15 (1917); Aronberg: *Astrophys. J.*, 47, 96–103 (1918); Harkins and Aronberg: 42, 1328–1335 (1920).

* The difference found by Harkins and Aronberg is not that predicted by the Bohr theory but is about fifty times larger.

[18] *J. Am. Chem. Soc.*, 37, 1383–95 (1915).

† A helium disintegration theory was suggested in 1913 by van den Broek, but his theory was much less definite, and was based upon the existence of a much larger number of elements.

The atomic weights of the light elements, taken together with their atomic numbers, give definite evidence that the nuclei of light atoms of even atomic number are built up almost wholly from alpha particles. Thus, beginning with carbon of atomic number 6, and up to iron of atomic number 26, the chemical atomic weight indicates that in every case the most abundant isotope has an atomic weight which is divisible by four, when the atomic number is divisible by two: that is both the mass and the charge are multiples by a whole number of those of the alpha particle, as is shown in Table III, in which *a* represents an alpha particle and *e* a negative electron.

TABLE III.

Evidence of the Atomic Weights and Atomic Numbers that the Nuclei of the Atoms of the Light Elements Are Built Up Largely of Alpha Particles.

Atomic Number.	Atomic Weight.	Composition of Nucleus Indicated.
6 = 3 × 2	12 = 3 × 4	a_3
8 = 4 × 2	16 = 4 × 4	a_4
10 = 5 × 2	20 = 5 × 4	a_5
12 = 6 × 2	24 = 6 × 4	a_6
14 = 7 × 2	28 = 7 × 4	a_7
16 = 8 × 2	32 = 8 × 4	a_8
18 = 9 × 2	40 = 10 × 4	$a_{10}e_2$
20 = 10 × 2	40 = 10 × 4	a_{10}
22 = 11 × 2	48 = 12 × 4	$a_{12}e_2$
24 = 12 × 2	52 = 13 × 4	$a_{13}e_2$
26 = 13 × 2	56 = 14 × 4	$a_{14}e_2$

The hydrogen-helium system may also be presented in the form of a table which gives the *composition* of the light atoms, as in Table IV.

It is of interest to note that this table was published four years before the discovery of isotopes among any of the light elements, with the single exception of the isotope of neon, whose existence was doubtful at that time. While the table was given the form of the chemical periodic system, it was specifically pointed out that the composition and stability of the nucleus are not related at all directly to this form of periodicity. The periodicity which is involved will be discussed later in the present paper, since it is of fundamental importance in connection with the study of the stability of atom nuclei.

TABLE IV.

The Helium-Hydrogen Composition of the Most Abundant Isotope of Each of the Light Elements as Presented in 1915 by Harkins and Wilson.

$H = 1.0078$.

	0.	1.	2.	3.	4.	5.	6.	7.	8.	
Ser. 2.	He He	Li $He+H_3$	Be $2He+H$	B $2He+H_3$	C $3He$	N $3He+H_2$	O $4He$	F $4He+H_3$		
Theor.	4.00	7.00	9.0	11.0	12.00	14.00	16.00	19.00		
Det.	4.00	6.94	9.1	11.0	12.00	14.01	16.00	19.00		
Ser. 3.	Ne $5He$	Na $5He+H_3$	Mg $6He$	Al $6He+H_3$	Si $7He$	P $7He+H_3$	S $8He$	Cl $8He+H_3$		
Theor.	20.0	23.00	24.00	27.0	28.0	31.00	32.00	35.00		
Det.	20.0	23.00	24.32	27.1	28.3	31.02	32.07	35.46		
Ser. 4.	A $10He$	K $9He+H_3$	Ca $10He$	Sc $11He+H$	Ti $12He$	V $12He+H_3$	Cr $13He$	Mn $13He+H_3$	Fe $14He$	Co $14He+H_3$
Theor.	40.0	39.00	40.00	45.0	48.0	51.0	52.0	55.00	56.00	59.00
Det.	39.9	39.10	40.07	45.1	48.1	51.0	52.0	54.93	55.84	58.97

Increment from Series 2 to Series 3 = 4He
Increment from Series 3 to Series 4 = 5He (4He for K and Ca)
Increment from Series 4 to Series 5 = 6He

It is evident that Table IV may indicate only that the light atoms have been *built up* largely from alpha particles (He nuclei), and that, taken alone, it does not prove that the alpha particles actually preserve their existence in the complex nuclei. The question of their presence in such nuclei will be discussed later.

12. THE NEW PERIODIC SYSTEM.

Classification of the Elements into (1) *Elements of Even Atomic Number,* and (2) *Elements of Odd Atomic Number.*

If only the most abundant isotope of each light element is considered, it is seen that the atom nuclei of the atomic species of even atomic number may be represented as built up of alpha particles, either alone or as the atomic weight increases, with the inclusion of (usually two) negative cementing electrons. However, it is apparent that this cannot be done in the case of the elements of *odd* atomic number, in which there is usually present a proton-electron *group* consisting of three protons and two electrons (p_3e_2), as is shown in Table V.

TABLE V.

Composition of Light Atoms.

(*Only the most abundant isotope of each element is represented.*)

Atoms of Even Nuclear Charge.						Atoms of Odd Nuclear Charge.					
At. No.	Symbol.	Formula of		Non-nuclear Electrons.		At. No.	Symbol.	Formula of		Non-nuclear Electrons.	
		Atom.	Nucleus.	Inner.	Valence.			Atom.	Nucleus.	Inner.	Valence
2	He...	He	a	e_2	..	3	Li ...	HeH_3	$a(p_3e_2)$	e_2	e
4	Be ..	He_2H	ape	e_2	e_2	5	B....	He_2H_3	$a_2(p_3e_2)$	e_2	e_3
6	C....	He_3	a_3	e_2	e_4	7	N....	He_3H_2	$a_3(p_2e)$	e_2	e_5
8	O....	He_4	a_4	e_2	e_6	9	F....	He_4H_3	$a_4(p_3e_2)$	e_2	e_7
10	*Ne*...	He_5	a_5	e_{10}	..	11	Na...	He_5H_3	$a_5(p_3e_2)$	e_{10}	e_1
12	*Mg* ..	He_6	a_6	e_{10}	e_2	13	Al ...	He_6H_3	$a_6(p_3e_2)$	e_{10}	e_3
14	*Si* ...	He_7	a_7	e_{10}	e_4	15	P....	He_7H_3	$a_7(p_3e_2)$	e_{10}	e_5
16	S	He_8	a_8	e_{10}	e_6	17	*Cl* ...	He_8H_3	$a_8(p_3e_2)$	e_{10}	e_7
18	A....	He_{10}	$a_{10}e_2$	e_{18}	..	19	K ...	He_9H_3	$a_9(p_3e_2)$	e_{10}	e_1
20	Ca...	He_{10}	a_{10}	e_{18}	e_2	21	Sc ...	$He_{11}H$	$a_{11}e_2p$	e_{18}	e_3
22	Ti....	He_{12}	$a_{12}e_2$	^{81}e	e_4	23	V....	$He_{12}H_3$	$a_{12}e_2(p_3e_2)$	e_{18}	e_5
24	Cr ...	He_{13}	$a_{13}e_2$	e_{18}	e_6	25	Mn. .	$He_{13}H_3$	$a_{13}e_2(p_3e_2)$	e_{18}	e_7
26	Fe ...	He_{14}	$a_{14}e_2$	e_{18}	e_8	27	Co...	$He_{14}H_3$	$a_{14}e_2(p_3e_2)$	e_{18}	e_9

It is evident that when only the most abundant isotope is considered there is a *periodicity of two* in the composition of the atoms, as contrasted with the periodicities of 8, 18, and 32 in the ordinary periodic system of Mendelejeff. This periodicity of 2 relates to the nucleus, while those of the ordinary system refer to the arrangement of the planetary electrons in the atom. Since the characteristics of the nucleus are not apparent in the chemical or physical properties of the elements with the exception of the property of mass, it is not to be expected that the periodicity here presented shall be apparent in any of the chemical or physical properties of the elements.

13. THE NEW PERIODIC SYSTEM AND THE STABILITY AND ABUNDANCE OF THE ELEMENTS.

The considerations involved in relating the above periodicity to the abundance of the elements will be presented in the form of a quotation from an earlier paper:

> It might be expected, however, that the composition of the nucleus should affect its own stability, which from radioactive evidence means the stability of the atom. From this standpoint it might be reasonable to suppose that the

atoms of one of the series, the even or the odd, should be more stable than those of the other. Now, unfortunately, there is no known method of testing the stability of the lighter atoms, but it might seem, at least at first thought, that the more stable atoms should be the more abundantly formed, and to a certain extent this is undoubtedly true. If then, at the stage of evolution represented by the solar system, or by the earth, it is found that the even-numbered elements are more abundant than the odd, as seems to be the case, then it might be assumed that the even-numbered elements are on the whole the more stable. However, there is at least one other factor than stability which must be considered in this connection. The formula of the even-numbered elements has been shown to be $n\text{He}'$. Now, since the formula for the odd-numbered elements is $n\text{He}' + \text{H}'_3$, it is evident that, if the supply of H_3 was relatively small at the time of their formation, not so much material would go into this system. This would be true whether the H_3 represents three atoms of hydrogen or one atom of some other element.[19]

In studying the relative abundance of the elements the ideal method would be to sample one or more solar systems at the desired stage of evolution, and to make a quantitative analysis for all of the ninety-two elements of the ordinary system. Since this is impossible, even in case of the earth, it might be considered that sufficiently good data could be obtained from the earth's crust, or the lithosphere.

However, there are several important factors which cause our knowledge of the quantitative composition of the earth's crust to be of much less value for the solution of our problem than it might seem to possess on first thought. In the first place the quantitative analyses which have been made represent the composition of only the mere skin of the earth, the depth of which does not exceed the ten to twenty miles caused by geologic displacements. The surface of the earth has been markedly influenced both by igneous processes which have resulted in magmatic differentiation, and by weathering, solution, and redeposition. For example, the common idea that sodium is a very abundant element undoubtedly has its origin in the fact that the solubility of its salts has caused their very considerable concentration in the oceans. Again, the fact that the salts of sodium are much more fusible than similar salts of the alkaline earths and most other metals in the rocks, has probably caused it to be segregated by magmatic solution and redeposition. Thus, while in the average igneous rock found on the surface of the earth there seems to be about 2.23 per cent. of sodium, it is not improbable that this is a larger percentage than would be found if the whole material of the earth could be taken as a sample for analysis.

If the sun is next considered it is found that although a large amount of its surface is exposed to us for spectroscopic investigation, the spectroscope gives no accurate measure of the quantitative composition, and that its findings are largely influenced by the height in the gaseous envelope of the sun at which the observation is taken.

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[19] The formula of the nucleus corresponding to H_3 is $(p_3e_2)+$ which would be an isotope of hydrogen. The ratio of negative to positive electrons in this group is 2/3, a much higher ratio than is found for any of the light atoms. This seems to indicate that the existence of independent nuclei of this type is improbable. Also Aston has failed to find any evidence of the existence of this isotope in hydrogen.

14. THE COMPOSITION OF METEORITES AS RELATED TO THE STRUCTURE OF COMPLEX ATOMS.

There is, however, material available of which accurate quantitative analyses can be made, and which falls upon the earth's surface from space. The bodies which fall are called meteorites, and no matter what theory of their origin is adopted, it is evident that this material comes from much more varied sources than the rocks on the surface of the earth.[20]

In any event, it seems probable that the meteorites represent more accurately the average composition of material at the stage of evolution corresponding to the earth than does the very limited part of the earth's material to which we have access. At least it might seem proper to assume that the meteorites would not exhibit any special fondness for the even-numbered elements in comparison with the odd, or *vice versa*, any more than the earth or the sun as a whole, at least not unless there is an important difference between these two systems of elements, which is just what it is desired to prove.

A preliminary study of the *most recent analyses* of meteorites of different classes showed that, either for any one class or for the meteorites as a whole, *the even-numbered or helium system elements are very much more abundant than those of the odd-numbered or helium-hydrogen system.* For a more detailed study use was made of the older but much more complete and more valuable data collected by Farrington,[21] who suggests that the average composition of meteorites may represent the composition of the earth as a whole.

The results obtained by averaging the analyses of 318 iron and 125 stone meteorites, 443 in all, show that the first seven elements in order of abundance are oxygen, iron, nickel, silicon, magnesium, sulfur, and calcium; and *not only do all of these elements have even atomic numbers, but in addition they make up 98.6 per cent. of the material of the meteorites.* Of the remaining elements present to a great enough extent to have an appreciable effect upon the percentage values, seven are odd and five are even, but in all only 1.22 per cent. are odd numbered, while 98.78 per cent. are even. Of the iron meteorites, 99.22 per cent. of the material is made up of even-numbered elements, and of the stone meteorites, 97.59 per cent.

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[20] Perhaps the theory of origin of the meteorites most in accord with their characteristics is that they are fragments of larger solid bodies, such as planets or planetesimals. Meteorites are known to vary in magnitude from the size of dust particles up to 36½ tons, though it is probable that much larger individuals than this maximum may have fallen. Their density varies from less than two to more than eight and one-half. In chemical composition they are much more closely related than the rocks on the surface of the earth, which seems to indicate that the parent bodies were much less affected by differentiative processes. If meteorites have been formed by the scattering of a very large body or bodies, it is evident that a relatively small portion of the material is derived from what may be called the crust, so that a very small part of the material would have been affected by weathering even if the parent bodies had atmospheres. However, whether this is true or not, evidence of weathering has not thus far been obtained. Meteorites may be classified in the three main divisions, iron, ironstone and stone meteorites, but much more elaborate classifications are found useful in showing the gradations by which one of these systems passes into the other. The fact that the substance of the iron and the stone meteorites passes gradually from one class into the other, that the nickel-iron and pyrrhotite of the stone is the same as that of the iron meteorites, and that the silicates of the stone meteorites gradually diminish in percentage amount as they grade over into iron meteorites, seems to suggest strongly that these different classes were originally present in some cosmic mass or masses, in which the materials were assorted according to their specific gravity. In such a body the lighter stony material would very probably be nearer the surface, and would therefore cool more quickly, while the nickle-iron would lie nearer the centre and would on this account cool very slowly. The physical properties of the two classes of meteorites seem to indicate that they have been cooled in just such a way.

[21] Farrington, *Publications* 120 and 151, Field Columbian Museum, Chicago, "Meteorites," 205 (1915); I, *Geol.*, 9, 623 (1901); Bvisse, *Mem. Soc. Lits. Sci. Arts l'Aveyron*, 7, 168; Meuner, "Cours. de Geol. Comparee;" Suess, "The Face of the Earth," (English translation), Vol. 4, p.543.

TABLE VI.

*Average Composition of Meteorites, Showing the Predominance of the Even-numbered Elements, and of the Elements of Low Atomic Number.**

		Percentage by weight. Stone meteorites.				Weight percentage. 53 stone meteorites.*		Atomic percentage. 125 stone meteorites.		Weight percentage.		Atomic percentage.		Atomic percentage. 318 iron meteorites.		Atomic percentage. 350 stone to 10 iron meteorites.†	
		125 analyses.		99 analyses.						Average of 318 iron and 125 stone meteorites.							
At. no.	Element.	Even.	Odd.	Even.	Odd.	Even.	Odd.	Even.	Odd.	Even.	Odd.	Even.	Odd.	Even.	Odd.	Even.	Odd.
1.	Hydrogen	...	..	...	..	..	0.084	...	..	...	..	..	...	...	..	...	..
2.		...	..	...	..	..	Trace	...	..	...	..	..	...	...	..	...	..
3.	Lithium	...	..	...	..	..	...	...	..	...	..	..	...	...	..	...	..
4.		...	..	...	..	..	...	...	..	...	..	..	...	...	..	...	..
5.		...	..	...	..	..	...	...	..	...	..	..	...	...	..	...	..
6.	Carbon	0.06	..	...	..	0.150	...	0.12	..	0.04	..	0.14	...	0.03	..	0.12	..
7.	Nitrogen	...	..	...	..	..	...	...	..	...	..	..	...	...	..	...	..
8.	Oxygen	36.02	..	35.82	..	36.290	...	54.70	..	10.10	..	25.87	...	...	..	53.16	..
9.	Fluorine	...	..	...	..	..	...	...	..	...	..	..	...	...	..	...	..
10.		...	..	...	..	..	...	...	..	...	..	..	...	...	..	...	..
11.	Sodium	...	0.59	...	0.70	..	0.645	...	0.62	...	0.17	..	0.30	...	..	...	0.62
12.	Magnesium	13.54	..	13.80	..	13.673	...	13.52	..	3.80	..	6.41	...	...	..	13.15	..
13.	Aluminium	...	1.39	...	1.45	..	1.527	...	1.25	...	0.39	..	0.59	...	..	...	1.21
14.	Silicion	18.41	..	18.18	..	18.154	...	15.79	..	5.20	..	7.53	...	...	..	15.35	..
15.	Phosphorus	...	0.06	...	0.11	..	0.113	...	0.05	...	0.14	..	0.18	...	0.17	...	0.06
16.	Sulfur	1.98	..	1.84	..	1.80	...	1.51	..	0.49	..	0.63	...	0.04	..	1.46	..
17.	Chlorine	...	..	...	..	..	0.080	...	..	...	..	..	...	...	..	...	..
18.		...	..	...	..	..	...	...	..	...	..	..	...	...	..	...	..
19.	Potassium	...	0.17	...	0.27	..	0.174	...	0.11	...	0.04	..	0.04	...	..	...	0.11
20.	Calcium	1.65	..	1.26	..	1.730	...	1.01	..	0.046	..	0.47	...	...	..	0.97	..
21.		...	..	...	..	..	...	...	..	...	..	..	...	...	..	...	..
22.	Titanium	0.01	..	...	..	0.108	...	0.005	..	0.01	..	0.005	...	...	..	0.005	..
23.	Vanadium	...	..	...	..	..	Trace	...	..	...	..	..	...	...	..	...	..
24.	Chromium	0.28	..	0.58	..	0.321	...	0.13	..	0.09	..	0.07	...	0.01	..	0.13	..
25.	Manganese	...	0.14	...	0.36	..	0.224	...	0.06	...	0.03	..	...	...	..	...	0.06
26.	Iron	24.32	..	24.32	..	23.313	...	10.57	..	72.09	..	52.93	...	90.64	..	12.79	..
27.	Cobalt	...	0.05	...	0.05	..	0.017	...	0.02	...	0.44	..	0.31	...	0.59	...	0.04
28.	Nickel	1.31	..	1.26	..	1.527	...	0.54	..	6.50	..	4.52	...	8.50	..	0.76	..
29.	Copper	...	0.01	...	0.01	..	0.014	...	0.005	...	0.01	..	0.005	...	0.02	0.005	..
	Total	97.59	2.41	97.06	2.94	97.022	2.978	97.89	2.11	98.78	1.22	98.575	1.425	99.22	0.78	97.985	2.105
		100%		100%		100%		100%		100%		100%		100%		100%	

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* 40, zirconium, none; 50, tin, none; 56, barium, none; elements 44, ruthenium; 46, palladium; 77, iridium; and 78, platinum, were found in stone meteorites, while 30, zinc; 33, arsenic; 51, antimony; 50, tin; 79, gold; 74, tungsten; and 92, uranium, were not found in the investigations reported by Merrill.

† It has been found by Farrington that the known falls of meteorites are in the ratio of 350 stone meteorites to 10 of iron.

The abundance relations in meteorites are exhibited graphically in Fig. 2, which gives the mean atomic percentages of the elements present in 350 stone and 10 iron meteorites, which is said to be the ratio of the known falls of these two classes.

It will be noted that in every case *the even-numbered elements are more abundant than the adjacent odd-numbered elements.* The rare gases of the atmosphere have been purposely omitted from the figure, since their physical and chemical properties are such that they could not be held by such small bodies as the meteorites, and the purpose of the diagram is to illustrate the general abundance relations of elements as nearly as is possible with the present limitations of knowledge. Table VI gives the average analyses of different types of meteorites as collected by different workers, and shows plainly that the predominance of the elements of even atomic number is not due to any selection of data. Even though the difference in the quantitative composition between the iron and the stone meteorites is very great, the atomic percentage of the elements of even atomic number is about 99 for the former and 98 for the latter.

15. THE PREDOMINANCE OF ELEMENTS OF EVEN ATOMIC NUMBER AS ILLUSTRATED BY THE COMPOSITION OF THE EARTH'S CRUST.

Since it has been shown that the elements of even atomic number are 70 times as abundant in the meteorites as those of odd atomic number, it should be of interest to see if the relations on the surface of the earth are at all similar. It should be remembered, however, that the crust of the earth is much more local in its character, and cannot therefore be expected to give such good evidence as that presented by the meteorites. It is found, however, that the elements of even number again show their predominance, since of the five most abundant elements, four have even atomic numbers, while of the first nine, six are even numbered, according to Clark's average for the composition of the lithosphere, as presented in Table VII.

The six even-numbered elements make up 85.74 per cent. of the lithosphere, while the three odd-numbered elements amount to only 12.77 per cent.

Table VIII gives another set of data for all of the elements as recalculated from a recent estimate made by Clarke and Washington.

The latter table shows that in the twenty top miles of the earth's crust the atoms of elements of even atomic number are about nine times as numerous as those of odd atomic number.

Since the data presented for the composition of the lithosphere suffer from the disadvantage for the present purpose, that the surface of the earth has been subjected to extensive processes of differentiation, it would be of extreme value if evidence could be obtained in regard to elements which have not been thus affected. While this cannot be done, it would seem that elements which are very much alike both chemically and physically should be affected more nearly to the same extent than those which differ widely. Now the rare earths are so similar that they are separated in the laboratory only with great difficulty, so the writer first made an estimate of the relative abundance of these elements, and then secured estimates made independently by two noted authorities, Profs. C. James and C. W. Balke. It is of interest that these three estimates were all in agreement. They are given in Table IX, in which c indicates common in comparison with the adjacent elements and r represents rare; ccc represents a relatively very common element, etc. The comparison is only a rough one, but it indicates that the even-numbered rare earths are much more abundant than the adjacent ones which are odd.

TABLE VII.

Abundance (percentage by weight) of the Elements in the Lithosphere, Illustrating the Predominance of Elements of Even Atomic Number.

Atomic Number.	Element.	Even	Odd.
8	Oxygen	47.33	..
14	Silicon	27.74	..
13	Aluminium	...	7.85
26	Iron	4.50	..
20	Calcium	3.47	..
11	Sodium	...	2.46
19	Potassium	...	2.46
12	Magnesium	2.24	..
22	Titanium	0.46	..
		85.74	12.77

The above results may be summarized in the statement that *in the formation of the elements much more material has gone into the elements of even atomic number than into those which are odd.*

16. THE UNKNOWN ELEMENTS.

Of the ninety-two elements within the limits of our present system, all but five have been discovered. It is of interest to note that all five *of the unknown elements have odd atomic numbers.*

TABLE VIII.

*Abundance of the Elements in the Crust of the Earth.**

(Atomic percentage for a twenty-mile crust.)

Order.	Element.	Atomic No.	Hydrogen.	Light Elements. Even	Light Elements. Odd	Heavy Elements. Even	Heavy Elements. Odd	
1.	Oxygen	8		57.44				
2.	Silicon	14		18.23				
3.	Hydrogen	1	9.48					
4.	Aluminium	13			5.55			
5.	Sodium	11			2.27			
6.	Iron	26		1.68				
7.	Calcium	20		1.68				
8.	Magnesium	14		1.59				
9.	Potassium	19			1.223			
10.	Titanium	22		0.273				
11.	Carbon	6		0.152				
12.	Phosphorus	15			0.093			
13.	Chlorine	17			0.088			
14.	Sulfur	16		0.052				
15.	Manganese	25			0.041			
16.	Fluorine	9			0.030			
17.	Chromium	24		0.024				
18.	Nitrogen	7			0.022			
19.	Vanadium	23			0.015			
20.	Lithium	3			0.014			
21.	Zirconium	40				0.012		
22.	Barium	56				0.011		
23.	Nickel	28		0.010				
24.	Strontium	38				0.007		
25.	Ce-Yt						(0.0037)†	
26.	Copper	29					0.0033	
27.	Glucinium	4		0.0019				
28.	Boron	5			0.0017			
29.	Zinc	30				0.0012		
30.	Cobalt	27			0.0010			
31.	Lead	82				0.0002		
	Total		9.48	81.1329	9.3487	0.0314	0.0033 (0.0037)†	100.00

0.000,0x
Rhubidium
Arsenic
Molybdenum
Tin
Bromine
Scandium

0.000,00x
Cadmium
Mercury
Iodine
Caesium
Antimony

0.000,000,x
Bismuth
Tungsten
Thorium
Cb-Ta
Uranium
Silver
Selenium

0.000,000,0x
Platinum
Tellurium
Gold

0.000,000,00x
Thallium
0.000,000,000,x
Indium
Gallium
0.000,000,000,0x
Germanium
0.000,000,000,000,x
Radium

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* Recalculated from a recent estimate by Clarke and Washington.

†In the analyses for these elements those of odd and those of even atomic number are reported together.

17. THE GREATER STABILITY OF RADIOACTIVE ELEMENTS OF EVEN NUMBER.

Among the radioactive elements it will be seen too that if the most stable isotope of each element is considered, then in each case the odd-numbered element has either a shorter period than the adjacent even-numbered elements, or else is entirely unknown. This is shown by Table X.

18. CLASSIFICATION INTO LIGHT ELEMENTS (ATOMIC NUMBERS 1 TO 27) AND HEAVY ELEMENTS (ATOMIC NUMBERS 28 TO 92).

It has been seen that an important natural classification of the elements with respect to their nuclear characteristics is into those of even and those of odd atomic number. A second important natural classification, introduced in 1915,[22] is into light elements up to atomic number 27, and heavy elements between atomic numbers 28 and 92. Of the latter elements 81 to 92 may be classed as specifically radioactive.

TABLE IX.

*The Predominance of Even-numbered Elements Among the Rare Earths.**

Atomic Number.	Abundance.	Element.	Atomic Number.	Abundance.	Element.
55	c	Caesium	63	rr	Europium
56	ccc	Barium	64	r	Gadolinium
57	c	Lanthanum	65	rrr	Terbium
58	cc	Cerium	66	r	Dysprosium
59	r	Praseodymium	67	rrr	Holmium
60	c	Neodymium	68	r	Erbium
61	rrr	Unknown	69	rr	Thulium
62	c	Samarium			

*Calcium and barium are also included in the table.

The classification was first made apparent by the mean atomic weights. It has been found that for the complex atoms of atomic numbers 2 to 27 the atomic weights are very close to whole numbers, with the exception of neon, magnesium, and chlorine (see Table II), and the exceptions were explained as due to the existence of considerable percentages of isotopes in these three elements.

It is very remarkable that while the atomic weights of the elements of numbers 19 to 27 are all very close to whole numbers, this approximation to whole numbers stops abruptly at this point, and from atomic number 28 to atomic number 80 the chemical atomic weights are practically as far from whole numbers as they should be from the standpoint of the laws of chance. It is also remarkable that for the heaviest or radioactive elements the mean atomic weights are again very close to whole numbers. It was pointed out by the writer seven years ago that the explanation of the above facts is that with the exception of neon, magnesium, and chlorine, isotopes do not occur in high percentages (in general not over 10 per cent. as a maximum) among the light elements, but beginning with nickel the number of isotopes and the distribution of the percentages of occurrence must increase. *Thus the region between atomic numbers 28 and 82 is one of many stable isotopes.* The general theory of the writer points out, however, that it is only among the even-numbered elements that the number of isotopes should increase very markedly in this region, since the number of isotopes per element should in general remain much lower when the atomic number is odd.

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[22] Harkins and Wilson: *J. Am. Chem. Soc.*, 37, 1386–96 (1915); Harkins: *Phys. Rev.*, 15, 79–94 (1920).

Table X.

Half Life of the Most Stable Isotope of the Radioactive Elements.

Atomic number.	Element.	One-half period of most stable isotope.	
		Even.	Odd.
92	Uranium	5 billion years	
91	Uranium X_2		1.15 min.
90	Thorium	18 billion years	
89	Actinium		Period unknown, but almost certainly less than radium
88	Radium	1730 years	
87			Element undiscovered
86	Niton	3.85 days	
85			Element undiscovered
84	Polonium	136 days	

Table XI shows that while the deviation of the atomic weights from a whole number is only 0.01 unit between atomic numbers 2 and 9, is 0.046 between 11 and 16, and only 0.07 between numbers 18 and 27, it rises to 0.247 from 28 to 37, and is also 0.247 between numbers 38 and 48. It should be noted that between atomic numbers 28 and 48 the average deviation from a whole number is almost exactly what it should be from the laws of chance. Thus an altogether random distribution of numbers would show a deviation of 0.250 from a whole number while each ten elements in this range show that the deviation is actually 0.247, which is almost the identical value for an entirely random distribution. The remarkable feature of the table is that it also shows that the large deviation from a whole number begins *suddenly* at nickel with a value of 0.32, is 0.43 for copper, 0.37 for zinc, etc.

Between atomic numbers 49 and 58 the deviation from a whole number becomes slightly smaller, and is thus a little less than is indicated by chance alone, the value being 0.229. Between atomic numbers 73 and 80 there is a further slight decrease to 0.214. However, the second remarkable feature exhibited is that between atomic numbers 81 and 92 the mean deviation falls to 0.102, or to much less than is indicated by a chance formation. This is due to the fact that while there are many isotopes of the elements 81 to 92, most of these isotopes are unstable, and in radium, thorium, and uranium, one isotope is in each case so much more stable than the others that the atomic weight of the element is practically that of the single most stable isotope.

19. THE ALPHA PARTICLE AS THE PRINCIPAL CONSTITUENT OF ALL ATOM NUCLEI, AND THE INDICATION THAT THERE ARE MANY ISOTOPES OF ELEMENTS OF EVEN ATOMIC NUMBER HIGHER THAN 28.

Table XII gives very definite evidence for considering that the alpha particle is the principal constituent of atom nuclei, and at the same time shows plainly that exactly at atomic number 28 where the atomic weights, as they increase, suddenly cease to be divisible by unity, they also cease to be divisible by 4, when the elements of even atomic number only are considered. This gives an additional indication that isotopes become numerous above atomic number 28.

While it is thus apparent that if the chemical atomic weights alone are considered, both the whole number rule, and the divisibility by 4 of the atomic weights of elements of even atomic number, seem to break down above atomic number 28, it is evident that this apparent invalidity of these rules is entirely illusive, since it is just among the heaviest or radioactive elements, that we have the direct experimental evidence that the elements change from one to another by the emission of alpha particles whose atomic weight is 4.00. Also, as noted in a previous paragraph, the whole number relation for the mean atomic weights appears to hold for the radioactive elements. Table XIII shows that the atomic weights of the radioactive elements of the uranium and thorium series are all even numbers.

It also exhibits the interesting relation that the atomic weight of helium, as derived by calculation from the chemical atomic weights of the radioactive elements, are as accurate, and also practically identical with those obtained from direct determinations.

TABLE XI.

Deviations of the Atomic Weights from Whole Numbers, Showing that for the Heavier Elements there is no Tendency for these Weights to Approximate Whole Numbers, while the Atomic Weights of the Elements below No. 28 are Extremely Close to Whole Numbers.

Few Isotopes.				Many Isotopes for Elements of Even Atomic Number.									
At. No.	Element.	At. Wt.	Diff. from Whole No.	At. No.	Element.	At. Wt.	Diff. from Whole No.	Probable Error in At. Wt.	At. No.	Element.	At. Wt.	Diff. from Whole No.	Probable Error in At. Wt.
2	He	4.00	0.00	28	Ni	58.68	0.32	0.02	49	In	114.8	0.2	0.5
3	Li	6.94	0.06	29	Cu	63.57	0.43	0.05	50	Sn	118.70	0.30	0.2
4	Be	9.017	0.017	30	Zn	65.37	0.37	0.05	51	Sb	120.2	0.2	0.3
5	B	10.9	0.10	31	Ga	70.1	0.10	0.5	52	Te	127.5	0.5	0.2
6	C	12.0025	0.0025	32	Ge	72.5	0.50	0.5	53	I	126.92	0.08	0.03
7	N	14.008	0.008	33	As	74.96	0.04	0.05	54	Xe	130.2	0.2	0.2
9	F	19.00	0.00	34	Se	79.2	0.20	0.1	55	Cs	132.81	0.19	0.05
Av. variation			0.039	35	Br	79.923	0.08	0.1	56	Ba	137.37	0.37	0.03
				36	Kr	82.92	0.08	0.1	57	La	139.0	0.0	0.3
				37	Rb	85.45	0.45	0.05	58	Ce	140.25	0.25	0.1
11	Na	23.00	0.00	Av. variation			0.247		Av. variation			0.229	
13	Al	26.97	0.03										
15	P	31.04	0.04						73	Ta	181.5	0.5	1.0
16	S	32.07	0.07						74	W	184.0	0.0	0.5
Av. variation			0.035						76	Os	190.9	0.1	0.4
									77	Ir	193.1	0.1	0.2
				38	Sr	87.63	0.37	0.03	78	Pt	195.2	0.2	0.1
18	Ar	39.9	0.10	39	Y	89.0	0.0	0.2	79	Au	197.2	0.2	0.1
19	K	39.10	0.10	40	Zr	90.6	0.4	0.2	80	Hg	200.6	0.4	0.4
20	Ca	40.07	0.07	41	Cb	93.5	0.5	...	Av. variation			0.214	
22	Ti	48.10	0.10	42	Mo	96.0	0.0	0.1					
23	V	51.00	0.00	44	Ru	101.7	0.3	0.1	81	Tl	204.0	0.0	0.2
24	Cr	52.00	0.00	45	Rh	102.9	0.1	0.05	82	Pb	207.20	0.20	0.1
25	Mn	54.93	0.07	46	Pd	106.7	0.3	0.1	88	Ra	226.0	0.0	0.1
26	Fe	55.84	0.16	47	Ag	107.88	0.12	0.02	90	Th	232.15	0.15	0.1
27	Co	58.97	0.03	48	Cd	112.4	0.4	0.03	92	U	238.16	0.16	0.1
Av. variation			0.070	Av. variation			0.247		Av. variation			0.102	

Note.—One of the remarkable features of this table is that the average deviation from a whole number is very low for both the light and the heaviest atoms, but is large between atomic numbers 28 and 80.

20. THE LIGHT ELEMENTS (ESPECIALLY THOSE WHOSE CHEMICAL ATOMIC WEIGHTS ARE DIVISIBLE BY 4) ARE ABUNDANT, THE HEAVY ELEMENTS ARE RARE.

The classification of elements into light and heavy is also of value in connection with the abundance of the elements. Thus about 99.9 per cent. of all known material consists of the elements of atomic number 1 to 28. In spite of the fact that according to the classification adopted in this paper there are twice as many heavy *elements* as of light elements, and probably four or five times as many heavy atomic *species* than of light species, only

TABLE XII.

Illustrates the Helium Structure of the Nucelei of Atoms.

<table>
<tr><th>Atomic Number.</th><th>Atomic Weight Divided by 4.</th><th>Deviation from a Whole Number.</th></tr>
<tr><td>2</td><td>1.00</td><td>0.00</td></tr>
<tr><td>6</td><td>3.00</td><td>0.00</td></tr>
<tr><td>8</td><td>4.00</td><td>0.00</td></tr>
<tr><td>10</td><td>5.04</td><td>0.04</td></tr>
<tr><td>12</td><td>6.08</td><td>+0.08</td></tr>
<tr><td>14</td><td>7.07</td><td>+0.07</td></tr>
<tr><td>16</td><td>8.01_5</td><td>$+0.01_5$</td></tr>
<tr><td>18</td><td>9.97</td><td>−0.03</td></tr>
<tr><td>20</td><td>10.02</td><td>+0.02</td></tr>
<tr><td>22</td><td>12.02_5</td><td>$+0.02_5$</td></tr>
<tr><td>24</td><td>13.00</td><td>0.00</td></tr>
<tr><td>26</td><td>13.96</td><td>−0.04</td></tr>
<tr><td colspan="3">Average deviation from a whole number up to this point is the extremely small amount of 0.026.</td></tr>
<tr><td>28</td><td>14.50</td><td>+0.50</td></tr>
<tr><td>30</td><td>16.34</td><td>+0.34</td></tr>
<tr><td>32</td><td>12.18_5</td><td>$+0.12_5$</td></tr>
<tr><td>34</td><td>19.80</td><td>−0.20</td></tr>
<tr><td>36</td><td>20.73</td><td>−0.27</td></tr>
<tr><td>38</td><td>21.91</td><td>−0.09</td></tr>
<tr><td>40</td><td>22.65</td><td>−0.35</td></tr>
<tr><td>42</td><td>24.00</td><td>0.00</td></tr>
<tr><td>44</td><td>25.42_5</td><td>$+0.42_5$</td></tr>
<tr><td>46</td><td>26.67_5</td><td>-0.32_5</td></tr>
</table>

Average deviation from a whole number for 10 elements beginning with element 28 is equal to 0.262, or almost what it should be by chance (0.250). *Notice that the break occurs exactly at element 28 (Ni), which is exactly the same element at which the atomic weights themselves cease to be close to whole numbers.*

about 0.10 per cent. of the material belongs to the heavy elements. Thus the ratio of abundance is of the order of one thousand to one in favor of the less numerous light elements.

While these facts have been known for a long period, as has been pointed out by Clarke, it had sometimes been considered that this was due to the sinking of the heavy elements to the centre of the earth, but has usually been left unexplained. The writer in 1917 presented evidence which seems to prove that *the explanation of these facts lies in the method by which the atoms were built, and by their stability relations.*

Table XIV gives the proportion by *weight* in which the heavy and light elements exist in different materials.

It is apparent that if the percentages were to be given in terms of the number of atoms, the abundance of the heavy elements would be very much less than that indicated in the table.

Thus *so far as the abundance of the elements is concerned the system seems to almost play out beyond atomic number 28, which is the last of the abundant elements.*

TABLE XIII.

Atomic Weights of Radioactive Atoms.

Atom.	Atomic Weight.	Deviation from a Whole Number.	Atomic Weight.
Uranium	238.175	+0.175	$59 \times 4.0030 + 2.00$
Thorium	232.12	+0.12	58×4.0023
Radium	225.97	—0.03	$56 \times 3.9983 + 2.00$
Radio-lead (Ra G)	206.07	+0.07	$51 \times 4.0014 + 2.00$

Table VIII shows that in the earth's crust *the number of atoms per light element is 5000 times as large as the number per heavy element.* Since there are many more isotopes of the heavy than of the light elements, the number of atoms per atomic species is extremely small above atomic number 28. It seems probable that on the average a light atomic species consists of 20,000 times as many atoms as a heavy atomic species. Since hydrogen and helium are the fundamental building blocks of the system, their abundance should not be and have not been included in such considerations as those presented above.

TABLE XIV.

Proportion in Various Materials of the Elements of Low Atomic Numbers.

	Percentage of elements with atomic numbers.	
	1-29	30-92
Meteorites as a whole	99.99	0.01
Stone meteorites	99.98	0.02
Iron meteorites	100.00	0.0
Igneous rocks	99.85	0.15
Shale	99.95	0.05
Sandstone	99.95	0.05
Lithosphere	99.85	0.15

21. PRIMARY AND SECONDARY FACTORS WHICH DETERMINE THE ABUNDANCE OF THE ELEMENTS.

It is evident from the preceding discussion that there is a direct relation between the abundance of the elements and the atomic number, and that there is no very marked relation to the periodic system of Mendelejeff. This indicates that the abundance of the elements is determined in a primary sense by the stability relations of the complex atoms themselves, and also by the stability of the electron-proton groups, such as the alpha particle, from which they are built. However, it is obvious, *even if in the formation of the elements there is no relationship to the ordinary periodic system, that in all of the differentiative processes which occur after the original formation, the chemical and physical properties would play their part, so that if any special material is taken for consideration, relationships to that system would appear more and more as the process of differentiation takes place.*

The fact that in the meteorites the elements of even atomic number are in all cases more abundant than the adjacent elements of odd number, seems to indicate that in such bodies the process of differentiation has not proceeded to such an extent as to cause the chemical and physical properties to have an influence sufficient to obscure in any marked degree the most general of the abundance relations due to nuclear stability, but it does not show that there has been an entire absence of differentiation. The composition of the earth's surface, as compared with that of the meteorites, shows a less rigid, but very marked adherence to the odd and even system, but certain groups of elements related in chemical and physical properties, are relatively more abundant. Thus the alkali metals, sodium and potassium, the halogens, and aluminium are present in much larger quantities. In the meteorites calcium is much less abundant than magnesium, while on earth both elements are of the same order of plentifulness.

22. THE GREAT STABILITY OF THE ALPHA PARTICLE DEDUCED FROM THE SPECIAL RELATIVITY THEORY.

That the alpha particle has a high order of stability seems to be shown by the fact that it holds together when emitted from radioactive nuclei at speeds as high as twenty thousand miles per second. Considerable interest has recently been manifested in the fact that the special theory of relativity also indicates its extreme stability, as was first shown by Harkins and Wilson[23] in 1915.

According to this theory one gram of mass is equivalent to 9×10^{20} (the square of the velocity of light) ergs of energy, or

$$E = mc^2$$

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[23] Harkins and Wilson: *Phil. Mag.*, 30, 731–3 (1915).

where E represents energy, m mass, and c the velocity of light. The change of mass involved in the formation of one gram atom of helium (4.000 grams) from 4 gram atoms of hydrogen (4×1.0078 or 4.0312 grams) is 0.0312 grams, so the energy change in the process should be

$$\Delta E = -0.0312 \times 9 \times 10^{20} = -2.808 \times 10^{19} \text{ ergs}$$
$$= -6.708 \times 10^{11} \text{ calories.}$$

Thus 6.708×10^{11} calories of energy are given off in the formation of 1 gram atom of helium, and this represents the free energy decrease. Now the free energy decrease in the formation of one mol of water from hydrogen and oxygen at atmospheric pressure is 57,000 calories, which is usually considered to be a large decrease. The magnitude of the change in the formation of one gram atom of helium is thus more than ten million times that in the formation of a mol of water.

The energy produced in this way would be of great importance if the reaction could be made to proceed, since one pound of hydrogen would give, if converted into helium, as much heat as 10,000 tons of coal.

This great amount of energy would be given off in the reaction

$$4\text{H} = \text{He},$$

but, since the two outer electrons are, even in the helium atom, attached very loosely in comparison with those in the nucleus, it is evident that the heat is practically all given off in the reaction

$$4\text{p} + 2\text{e} = \text{p}_4\text{e}_2,$$

that is in the formation of the alpha particle from four protons and two electrons.

While nothing is known of the conditions under which this reaction takes place, it is possible that it occurs at high temperatures, or at high pressures, or when both the pressure and the temperature are high. *The occurrence of the reaction in the stars, or the sun, would be a possible source of the heat of these bodies,* which seems to be in excess of any amount which could be obtained by purely physical or chemical changes.

At first thought it seems remarkable that a reaction which would liberate such an extremely large amount of energy, does not occur at a detectable rate in ordinary hydrogen gas at moderate temperatures. However, this is only a more marked example of what is found in the union of hydrogen with oxygen at ordinary temperatures. While the free energy of this latter reaction is high, it does not occur at a measurable rate. In the formation of the alpha particle six electrons are involved, and it is probable that these electrons, four positive and two negative, must arrange themselves in a definite configuration before an alpha particle is formed. Thus the chance that this particular arrangement will occur is very slight, so that the reaction is a very slow one, at least under ordinary conditions.

23. A MODEL FOR THE ALPHA PARTICLE.

The most important condition which must be met by any successful model of the alpha particle is that it must give an explanation of the packing effect, amounting to 0.77 per cent. decrease when the four protons and two electrons unite. A decrease in mass indicates that in the alpha particle the positive electrons must be very close to the negative electrons, in order that the mass of the former shall be decreased by about the above percentage. The mass of the negative electrons is so small already before the combination, that any decrease in their mass cannot contribute in any large way to the total effect. It has already been mentioned that if the inverse square law were to hold at such minute distances, the charges on the positive and negative electrons would need to be displaced or else the positive electrons would need to be imbedded in the negative electrons, to give a loss of mass of such a considerable magnitude. However, it seems probable that the inverse square law does not hold, and that the law of force changes rapidly, the power increasing, as the electrons approach each other very closely.

The greatest difficulty in constructing such a model is that we are ignorant of the distribution of electricity in electrons, their form is unknown, and the relative sizes of the negative and positive electrons are undetermined. If the Lorentz form of electron, and the inverse square law in the electron itself, are assumed, the positive electron should have a diameter only 1/1835 that of the negative, since the mass of the former is 1835 times larger (Equation 2, Section 7). Using this general result as a basis, the model of the alpha particle adopted by the writer[24] assumes that the positive electron is smaller than the negative electron, but not necessarily as much smaller as equation 2 indicates.

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[24] *Phys. Rev.*, **15**, 82, February (1920). (Paper presented in May, 1919.)

While the positive electrons must be very close to the negative to give the packing effect, it is evident that the positive electrons themselves cannot be close to each other, since any such proximity would mean a considerable *increase* of mass, while the packing effect is a decrease. Fortunately, with large electrons and small protons it is possible to construct a model in which the protons are relatively far apart, but with the electrons and protons very close together. Such a model is presented in Fig. 3.

24. THE MASS AND ENERGY EVOLVED IN THE DISINTEGRATION OF RADIOACTIVE SUBSTANCES.

In the last section the energy evolved in the formation of one gram atom of helium was calculated from the mass change involved, in the present section the converse problem will be treated, the calculation of the change of mass from a change in energy for each radioactive series, the end product in each case being lead. The total energy change per gram atom of lead formed is about 0.05 gram, or about 66 per cent. greater than that in the formation of one gram atom of helium, but it should be considered that the total mass involved is more than 50 times as large in the case of the radioactive substances. Also seven or eight alpha changes occur in each radioactive series, and it is the total mass change for all of these which is given above. The first calculation of this nature was made by Swinne[25] in 1913. The calculations given here were made two years later by W. D. Turner and the writer from data[26] published in 1914.

The amount of energy given off in an alpha disintegration may be calculated by the method given below, and this may be checked in some cases by comparison with the results obtained in direct calorimetric measurements. The energy involved in beta disintegrations is relatively so small that it may be neglected. The initial velocity (v) of an alpha particle may be calculated from the range (R) by the equation of Geiger[27]

$$v^3 = aR \tag{1}$$

where a is a constant.

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[25] Swinne: *Physik. Z.*, **14**, 145 (1913).

[26] *Le Radium*, 1914.

[27] Geiger: *Proc. Roy. Soc.* (A), **83**, 505 (1910).

The value of the constant a has been found to be 1.33×10[28] by measurements on radium C.

Now

$$E_{,}=\tfrac{1}{2}\, mv^2 \tag{2}$$

so from (1)

$$E_{,}=\tfrac{1}{2}\, m(aR)^{2/3} \tag{3}$$

in which m, the mass of the alpha particle, is 6.6×10^{-24} grams.

To this must be added the energy of recoil of the disintegrating atom, which may be calculated on the basis that its momentum is equal to that of the alpha particle.

$$MV=mv \quad \text{so } \tfrac{1}{2}\, MV^2=\frac{m}{M}\cdot \tfrac{1}{2}\, mv^2=\frac{m}{M}\cdot E' \tag{4}$$

Therefore the total emission of energy per alpha particle is

$$E'=\left(1+\frac{m}{M}\right) E_{,} \tag{5}$$

$$E'=\left(1+\frac{m}{M}\right) \tfrac{1}{2}\, m\,(aR)^{2/3} \tag{6}$$

The number of alpha particles given off in the disintegration of a gram atom of a radioactive substance by one alpha change, is 6.06×10^{23}, so the energy per gram atom of helium emitted is

$$E=6.061\times 0^{23}\ E'=6.06\times 10^{23}\left(1+\frac{4.00}{P}\right) \tfrac{1}{2}\ \frac{4.00}{6.06\times 10^{23}}\,(aR)^{2/3}$$
$$=2.42\times 10^{18}\left(1+\frac{4}{P}\right) R^{2/3}\,. \tag{7}$$

The energy evolved per gram atom of substance per second (E_0) is the product of the energy per alpha particle times the number (N) of alpha particles given off per second, plus the correction for the recoil atom:

$$E_0=N\left(1+\frac{m}{M}\right) E_{,}=NE' \tag{8}$$

With E_0 known, the total energy emitted ΔE during the entire transformation may be found from the radioactive constant (λ) by means of the equation:

$$\Delta E=E_0/\lambda \tag{9}$$

From the value of the energy the equivalent in mass may be calculated by the equation of Einstein.

$$M=\frac{\Delta E}{9\times 10^{20}}. \tag{10}$$

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[28] Rutherford: "Radioactive Substances," p. 582.

25. EXPERIMENTAL TESTS OF THE SPECIAL RELATIVITY THEORY.

Since the loss of mass between uranium and lead amounts, according to these calculations from the relativity theory, to about one-twentieth of a gram, it is obvious that this part of the theory is susceptible to experimental test, since if atomic weight determinations could be made on both uranium and radium G, or on thorium and thorium-lead, with an error of less than one one-hundredth unit, the difference between the two extreme atomic weights should be equal to 32.05 in the former, and 24.04 in the latter, of the two cases. Since no atomic weights have as yet been determined in the actinium series, checking up the use of the calculated difference in this series with that determined experimentally does not look so hopeful. Since most of the loss of mass in the radium series occurs between radium and radium G (lead

Table XV.

The Change of Mass During the Disintegration of Radioactive Svbstances.

Atomic Species	Atomic Weight	Range R	Change of Energy in Ergs x 10^{-18}	Change of Mass.	
			Uranium Series		
Uranium I	238	2.37	4.27	0.00475	
Uranium II	234	2.75	4.83	0.00536	
Ionium	230	2.85	4.94	0.00549	
Radium	226	3.13	5.86	0.00585	
Emanation	222	3.94	6.14	0.00682	
Ra A	218	4.50	6.71	0.00746	
Ra C′	214	6.57	8.80	0.00977	
Ra F	210	3.58	5.77	0.00641	
Total loss of mass: uranium to lead					0.052 grams
			Thorium Series		
Thorium	232	2.58	4.63	0.00514	
Radiothorium	228	3.67	5.86	0.00651	
Thorium X	224	4.08	6.28	0.00698	
Th emanation	220	4.74	6.94	0.00772	
Thorium A	216	5.40	7.58	0.00842	
Thorium C′	212	8.16	9.98	0.01110	
Total loss of mass: thorium to lead					0.046 grams
Thorium C	212	4.55	6.76	0.00752	
Total loss of mass: thorium to lead					0.042 grams
			Actinium Series		
Protoactinium	230?	3.5	4.48	0.00500	
Radioactinium	226	4.36	6.57	0.00730	
Actinium X	222	4.17	6.38	0.00709	
Ac emanation	218	5.40	7.58	0.00842	
Actinium A	214	6.16	8.28	0.00920	
Actinium C	210	5.12	7.32	0.00814	
Total: protoactinium to lead					0.045 grams
Total loss of mass: uranium to lead (provided series comes from U_{II}) about					0.054 grams

206), it would be possible to use the atomic weights of these two elements instead of those of uranium and radium G.

A more direct, but less hopeful method experimentally, on account of the too costly initial investment and the scarcity of materials, would be to seal up in a glass and then in a metal tube, a sample of radiothorium or mesothorium, or some other very radioactive substance, and to detect the loss of mass by weighing the tube with extreme care at long intervals of time. In order that the time might not be too long, the amount of mesothorium taken should be considerable. The tube would need to be provided with a sealed-in conducting wire in order to prevent the accumulation of a charge, but the preservation of a gas-tight seal could be insured by a careful sealing of the platinum outside tube. If alpha particles and helium gas were prevented from escaping, a loss of mass of the tube and its contents would be a qualitative test of the theory of relativity. By carefully determining the amount of radioactive material in the beginning, the test could be made quantitative. The difficulty of the experiment lies in the fact that with ten grams of radium it would take about 1800 years to get a loss of mass of one milligram. While the same amount of radiothorium would give this loss of mass in three years, radiothorium is very much more rare, though cheaper in proportion to its activity, than radium.

The tests of the special relativity theory here outlined involve the assumption that the energy involved comes entirely from the atoms, and that it is not supplied to the atoms during the experiment in the form of some penetrating radiation or otherwise.

(To be continued.)

On a New Type of Transformation in Iron. G. BORELIUS and F. GUNNESON, University of Lund. (*Ann. d. Physik*, No. 3, 1922.)—We have alpha, beta and gamma rays and there was a time when there were N-rays too, though they have ceased to exist. X-rays are with us for all time, and now here are two papers to convince us that there are Z-transformations in iron. How are these transformations detected? By a study of the thermo-electric powers of the specimens under examination.

A piece of iron wire was heated in an electric furnace, then promptly cooled by dropping in water. After this its thermo-electric power at room temperature was measured. A similar piece was thereupon heated to a somewhat higher temperature, cooled and its power measured, and so on. When the temperatures are plotted as abscissas and the thermo-electric powers as ordinates a series of waves manifest themselves. From a long series of observations it appears that the presence of certain appropriate substances in the iron augments the amplitude of the waves. Electrolytic iron, heated for hours in an atmosphere of illuminating gas, furnished waves of especially great amplitude; while the same kind of iron, melted in a vacuum to form an alloy containing 5 per cent. silicon, gave a smooth curve. Heating the specimen in gas, however, made the waves appear.

Not only are there waves, but they are rather regular waves, so regular in fact, that if we agree to recognize each of them as indicating a modification of the iron, it may be said that the middle temperature of each transformation interval is computed in absolute degrees by multiplying the ordinal number of the transformation by 97. If we take the tenth transformation, we thus get for its temperature 970° abs., which is just about the perlite or Curie point. Perrier and Wolfers at the general meeting of the French Physical Society, January 21, 1921, presented a method of detecting transformations in substances, and state that there is an anomaly in iron at 1140°. If 273° be added to this to change to absolute degrees the sum is 1413, which is about midway between 14 and 15 times.

There had previously been reason to infer that strange things happen to iron in addition to the fully recognized and catalogued transformations. Roberts-Austen of the British Mint and A. Mueller noticed that electrolytic iron with a high content of hydrogen, upon heating, gives up the gas, not gradually, as one would expect, but only at certain temperatures. Moreover the density of a certain steel has been found to be a periodic function of the temperature of tempering. With a wider view Robin detected a connection between temperature and tensile strength, hardness and elasticity that pointed toward transformations. Certain magnetic relations tend to confirm this conclusion.

It has been mentioned that silicon, which forms a stable solid solution with iron, does not incite to transformation, while carbon does favor such changes. There is yet no definite experimental evidence to show in what the transformations consist, though the suggestion is made that we must look to the space lattice of the metal for the answer.

At the meeting of the Strasbourg Section of the French Physical Society, December 16, 1921, the president of the parent society, Paul Janet, presided. Langevin in his discussion of "The Dynamics of Relativity," said the following: "The theory of relativity is the only theory which takes into account all the facts of physics actually known and which from them makes possible the prediction of new facts. In particular in the domain of limited relativity, that is, in the absence of a gravitational field, it leads to a new system of dynamics where the mass of a body ceases to be a constant and varies not only with the velocity of the body, but also with its interior state, where, further, the conception of mass merges with that of internal energy.

G. F. S.

THE FIRE-FLY AS AN ILLUMINANT.*

BY

HERBERT E. IVES, Ph.D.

Member of the Institute.

INTRODUCTORY.

The purpose of this paper is to review the results of a series of studies made some years ago on the physical properties of the light emitted by the fire-fly. As these studies appeared in several different scientific and technical journals, their essential unity of object has perhaps been somewhat obscured. Together they constitute practically the first, and even at this date the chief, definite *quantitative* data on the radiant emission of the fire-fly considered from the standpoint of the illuminating engineer; that is, covering such essential points as efficiency and intensity. More accurately determined figures for the fundamental constants of illumination are now available, so that in assembling and reviewing the original fire-fly data it has been possible to establish with greater exactness their significance in connection with practical light production. Some variations on the method of treating the subject in the original communications have also appeared desirable upon considering the matter as a whole, and have accordingly been introduced.

SIGNIFICANT CHARACTERISTICS OF AN ILLUMINANT.

The most important questions to be answered in studying an illuminant are three: *How much* light does it produce; how *efficiently* does it produce the light; what is the *quality* of the light? Let us consider each of these attributes briefly.

The *quantity* of light which could be got from an artificial source was undoubtedly the first problem of the first illuminating engineer. He cared nothing about efficiency in the physical sense; " hot light " was just as acceptable to him as " cold light " (often even more acceptable). There must be enough light to scare off wild animals, to illuminate the approaches to camp or cave, to make possible the performance of simple mechanical operations such as preparing weapons or implements for hunting. If his camp-fire, torch, or flaring wick floating in grease gave an adequate quantity of light it sufficed, irrespective of efficiency or color.

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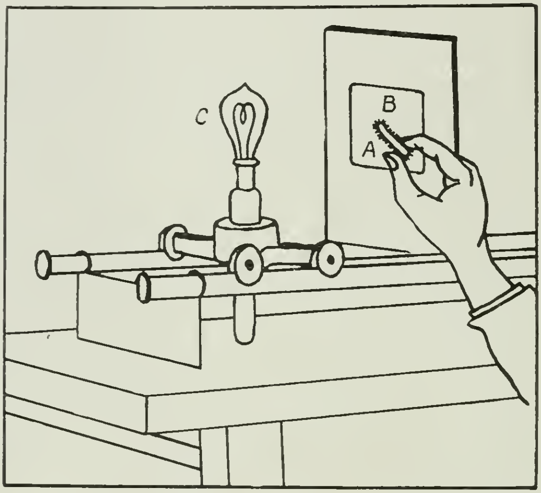
* Communicated by the Author.

But the requirement as to quantity is not quite so simple as it may have appeared to primitive man. It might well have happened that a fire bright enough to see by would have been too hot to sit by. It might well have happened that a torch bright enough to light his way would have been too heavy to carry. It might well have happened that his sole light source at night would have been only bright enough, no matter how large it was made, to be seen, and not bright enough to see by, as is actually the case with certain phosphorescent glowing bacteria. It therefore becomes obvious that the *size* of the light source must be considered as well as its total emission. It is in fact with the relation of light emission to emitting area that the lighting engineer is concerned. The physical quantity of significance is the *specific luminous emission*, or luminous emission per unit area, measured in *lumens per square centimetre.* If this falls below a certain minimum the light source is unavailable for purposes of illumination. If it exceeds this minimum, but is low, the source will be available only where space is ample, and when portability is not essential. If the specific emission is high, it becomes possible to construct an illu-

FIG. 1.

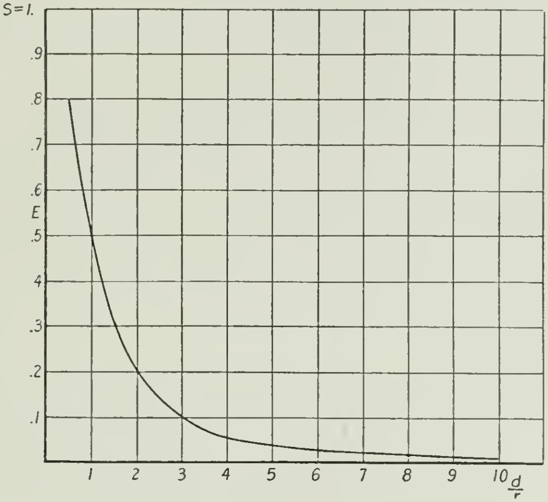


Method of measuring the light of the glowworm.

minant, compact in size, whose luminous emission is susceptible of direction or diffusion. It is illuminants of this latter class that have played the greatest rôle in artificial lighting; their admirable flexibility does not, however, entirely close the field to light sources of low specific emission should those latter possess other claims to use, such as high efficiency.

Considering now *efficiency;* primitive man knew nothing of luminous efficiency in the physical sense; he was concerned with efficiency only from the standpoint of the cost of his materials, and until recent times the cost of the wood, tallow or oil used in fabricating the light source counted little against the boon of having any sort of useful light at night. This condition of affairs is indeed still largely true, but scientific study has revealed that the ordinary processes of light production are criminally inefficient when we measure the ratio of light yielded to energy put in. Any process in which a representative figure for efficiency is one per cent., as is the case in light production, is an anomaly and a challenge to present-day engineering.

FIG. 2.



Illumination due to circular disc of diffusely radiating material of specific luminous emission *S*, at various ratios of distance (*d*) to radius (*r*).

The measurement of the efficiency of light production may logically be undertaken in two steps. The first step is to determine the efficiency with which the energy supplied is transformed into radiant energy—*the radiational efficiency*. The second step is to determine the *radiant luminous efficiency;* that is, how efficient is this radiant energy as light—does it lie in the visible spectrum, and how advantageously is it placed in the visible spectrum? The product of these two efficiencies is called the *total luminous efficiency*. The radiational efficiency of a light source may run above 90 per cent., as it does in the case of a vacuum incandescent electric lamp. Flame-heated radiants such as a Welsbach mantle lose so much heat by convection that their radiational efficiency falls as low as 50 or even 25 per cent. It is, however, in the luminous efficiency of the radiation that all practical illuminants are so badly deficient. Measured against the most advantageously placed radiation—a monochromatic patch in the yellow-green of the spectrum—the radiation from the most efficient incandescent illuminants falls below five per cent. efficiency. Efficiencies of light production, properly expressible in percentages, are commonly obscured by the different units used in stating energy input and luminous energy output. *Lumens per watt,* the practical measure, may be transformed to percentage efficiency by using the relation that the maximum possible (100 per cent.) efficiency is 640 lumens per watt.

Quality of light is a matter of the distribution of the radiation through the visible spectrum. If the spectrum is continuous, and if the radiant intensity is nearly the same at all wave-lengths, the light is "white." The colors of objects illuminated are seen in their true (*i.e.,* their daylight) values; the light is pleasant. If the spectrum is continuous but much more intense toward the long wave (red) end, the light will appear yellow, but may still be agreeable in integral color; illuminated objects will be distorted from their daylight color values, although usually maintaining their same relative position on a color scale. This is the type of spectral energy distribution presented by the great majority of artificial illuminants, such as flames and glowing filaments. If the spectrum is discontinuous, so that only certain regions of the spectrum are present, the light may appear of any integral color, including white, depending on the relative intensities of the constituents; it may or may not be pleasant as an illuminant. Color values of illuminated objects will then be distorted in more or less peculiar ways, depending on the coincidence or lack of coincidence of the wave-lengths which are present in the light and reflected by the object. If the spectrum of the light is so discontinuous as to be monochromatic, the deficiency of color-rendering capacity may be offset for certain purposes, by a useful property possessed in greater degree by monochromatic illumination than by continuous spectrum illumination of the same intensity; this is the property of rendering visible fine details. *Visual acuity* is considerably greater by monochromatic light, and is also notably higher for the middle (green) of the spectrum, than for the ends (red and blue).

We are now ready to consider in detail the fire-fly, as an illuminant, taking up in order its specific luminous emission, its efficiency, the quality of its light.

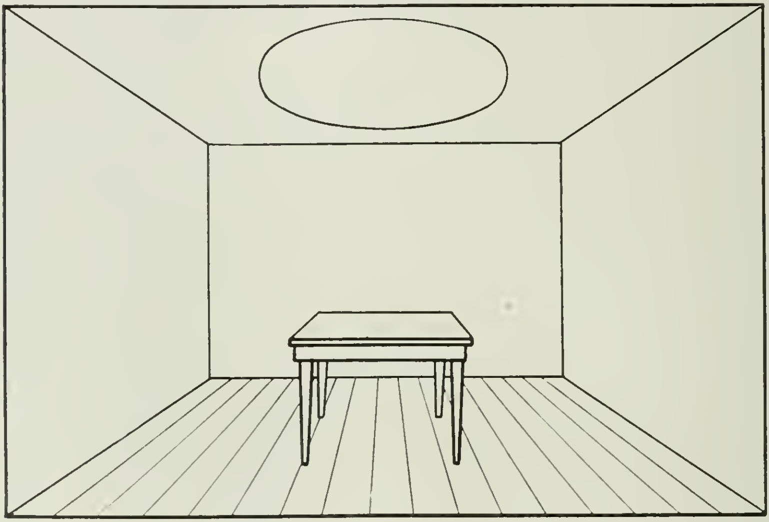
SPECIFIC LUMINOUS EMISSION OF THE FIRE-FLY.

We must not be misled by the small amount of light given out by a single fire-fly flash, particularly the flash of the small insect of the eastern and northern United States. The large Jamaica variety has been estimated by W. H. Pickering[1] to give a flash of .004 candle-power, a figure arrived at by comparing its flash with stars of various magnitudes. At first sight the idea of using lighting units of this size for practical illumination appears wild enough to discourage further study. But as already noted we must take into account the area from which the light is emitted. For these large tropical fire-flies the luminous area is about one and a half square centimetres. If the luminous portion is assumed to be a plane, the specific luminous emission (πx candle-power per unit area) works out as

$$\frac{.004}{1.5} \times \pi = .0084 \text{ lumens per square centimetre.}$$

This is a figure which we could use if necessary. It is not entirely satisfactory, because of uncertainties due to comparing intermittent and steady lights. Furthermore, even should this specific luminous emission prove to have practical value, the fact that the light is only available in widely separated flashes might well make us pause before drawing conclusions as to the real efficiency of the process. Indeed, were the intermittent character of the fire-fly's light proved to be fundamental and inevitable, it would be questionable whether its further study would be worth while from our standpoint. Fortunately for the fate of the whole problem, and for the particular problem of measurement, the *larva* of the fire-fly gives a continuous steady glow of very nearly, if not quite the same, quality as the flashing light, not so bright as the isolated flashes, although very probably of nearly the averaged value of these. This steady larval light is much more suitable for measurement, analysis, and ultimate copying, if that be possible or desirable, than the more spectacular performance of the adult creature. The rather exact measurements of specific luminous emission which are described below [2] were made on specimens of the larva of one of the Pennsylvania varieties of fire-fly, much smaller, although perhaps intrinsically just as bright (*i.e.*, as intense per unit emitting area) as the more famous West Indian varieties.

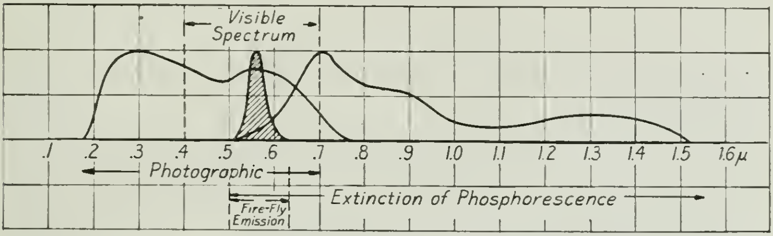
FIG. 3.



Illumination of room by diffusely radiating disc at ceiling.

The method of measuring the luminous emission of the larva or glow worm is illustrated in Fig. 1. It was noticed that the light-giving portion of the glowworm, located on its abdomen, could be so turned as to be on the extreme edge of its profile. If then the worm was held in front of a large bright area, this luminous spot together with the background formed the two parts of a simple photometric field. In the diagram *A* is the glowworm, held between thumb and forefinger; *B* is a white diffusely reflecting surface illuminated by the standard lamp *C*, whose distance from *B* is adjustable (the glowworm was of course shielded from the direct light of the lamp by screens not shown in the figure). The process of measurement consisted in varying the position of the standard lamp until the glowworm and the white surface appeared equally bright. Although there is a considerable difference in color between the standard (carbon incandescent lamp) and the glowworm, settings were made without difficulty. The result of the experiment gave as the mean value of the illumination of the white surface (calculated by the inverse square relation from the distance of the standard lamp) necessary to match the luminous glowworm abdomen the figure 190-metre candles, or *.0190 lumens per square centimetre.*

FIG. 4.

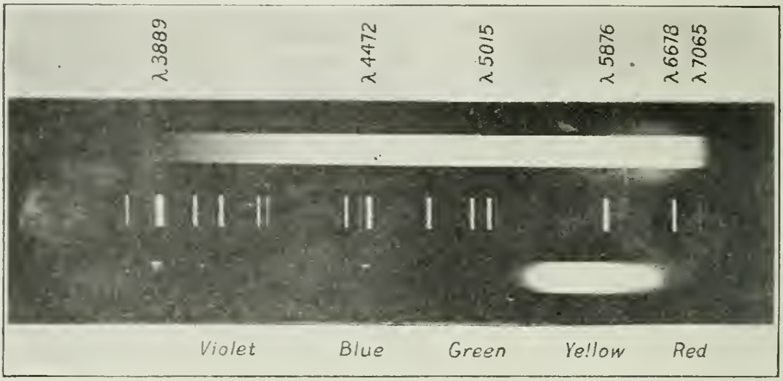


Regions of the spectrum covered by photography and extinction of phosphorescence.

In order to reduce this to lumens emitted per square centimetre we must first correct for the reflecting power of the white blotting paper which was used at *B*, namely, 76 per cent. Applying this we get for the specific luminous emission of the white surface, .76 × .0190 = .0144 lumens per square centimetre.

Thus far the experiment merely tells us that *when viewed in a certain direction* the emission from a certain area of the glowworm *which is seen in projection* matches a diffusely emitting plane surface whose emission is .0144 lumens per square centimetre. In the experimental work there was no indication that the glowworm's emission was other than diffuse; that is, that the photometric match would not hold for any direction, so that the first qualification may be dismissed. But the matter of determining the true area of the emitting portion whose projection we observe is not so easy. If the luminous portion were a flat plate then the specific luminous emission would be exactly that of the illuminated blotting paper background. If the luminous portion were a hemisphere, the quantity in question, according to relations derived from the theory of radiating surfaces, would be half that of the flat background; if half a cylinder, it would be $\frac{2}{\pi}$ times that of the background. The luminous abdomen of the insect is actually composed of a series of overlapping plates of convex curvature; the curvature is small, however, so that no serious error will be introduced in assuming them to be equivalent to a single flat plate. We shall, therefore, in what follows, adopt for the *specific luminous emission of the glowworm,* the figure given directly by the experiment, namely *.0144 lumens per square centimetre,* merely bearing in mind that the true figure is probably a little lower. It may be noted that this value is of the same order of magnitude as that derived from Pickering's estimate of the intensity of a single flash.

FIG. 5.

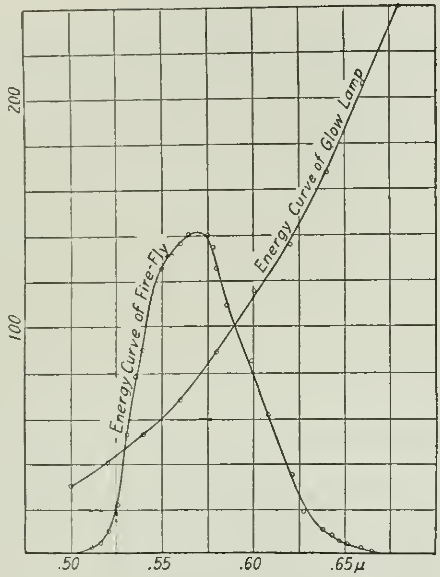


Spectrogram of fire-fly light (lower spectrum), carbon incandescent electric lamp light (upper spectrum), helium vacuum tube (middle spectrum).

Let us now consider this figure. Compared with the 500 of the tungsten filament or the 1.0 of a typical sky, it appears excessively low. This does not necessarily mean that it is too low to be useful, because most of our artificial light sources are of such high specific emission that their brightness must be reduced by the use of diffusing glassware or reflecting surfaces. Does it indeed still lie in the range of usefulness, or is the glowworm like those markers of phosphorescent radium containing material, which can be seen but which are too weak to give useful illumination?

We can answer this question by considering the illumination due to an *extended luminous surface,* for obviously a "point" source of only $\frac{1}{30,000}$ the intensity of a tungsten lamp would be too weak for any use. Now it may be shown that if we take a diffusely-radiating disc of specific luminous emission S, and of radius r, the illumination on a point in its axis, at distance d is

FIG. 6.



Energy distribution in radiation of fire-fly.

$$E = S\left(\frac{1}{1+\frac{d^2}{r^2}}\right)$$

where E and S are expressed in the same units of area, *i.e.,* if S is in lumens per square centimetre, E also refers to square centimetres. For points off the axis E becomes smaller, but slowly enough so that we need not here take the decrease into account. The relation between E and $\frac{d}{r}$ is shown in Fig. 2. Let us at once substitute for S its value as determined from experiment, and in order the more quickly to correlate the result with practical illumination figures, let us express it in lumens per square metre (metre candles). Taking the resultant figure, 144 lumens per square metre, we can compute at once from Fig. 2 that at $\frac{d}{r} = 1$ the illumination will be 72 lumens per square metre, at $\frac{d}{r} = 2$, it will be 29 lumens per square metre, at $\frac{d}{r} = 3$ it will be 14 lumens per square metre, etc.

It now only remains to compare these with illuminations which have been found satisfactory for various practical locations and occupations. A representative table is here reproduced.[3]

Illumination for Various Purposes.

	Meter Candles
Reading, U. S. Government Post Office minimum requirements	30
Clerical and office work	32–75
Drafting	50–100
Factory work, coarse	15–30
Factory work, fine	30–100
Corridors	3–10
Audience rooms	10–30

It will be seen that our figure for $\frac{d}{r} = 2$, namely, 29-metre candles, lies in the midst of these. It would be satisfactory for those cases which may be classified as general illumination. What does this mean in terms of space requirements? This is simply shown in Fig. 3, where, as a typical case, a room three metres in height is chosen with a central table at a height of one metre. Upon the ceiling is placed a disc of luminous material two metres in diameter. From our calculations it follows that the illumination on the table from such a ceiling panel would be quite adequate for many purposes. Increase in the size of the luminous ceiling panel, keeping the height the same, will increase the illumination up to a limit (for an infinitely large room) of 144-metre candles, which is well above any of the requirements set forth in the above table. This scheme of illumination will be recognized as identical with "deck lighting" or with the so-called "indirect" system, in which the effective light source is the bright ceiling.

The net result of this study thus shows that while the specific luminous emission of the glowworm is not of such a magnitude as to recommend its use for locomotive headlights or for intense local lighting, it is, as it stands, of practical intensity for use in methods of lighting now in vogue. The *flash* of the ordinary fire-fly is much more intense than the glow of its larva, so that it is reasonable to suppose that the same process of light production would be capable of speeding up so as to require less space than is used in the manner shown in Fig. 3, practical though that arrangement is.

EFFICIENCY.

Knowing the specific luminous emission of the luminous organism we could at once obtain its *total luminous efficiency* if we knew the rate of consumption of energy or work per unit of luminous area. We would then have its lumens per watt, directly reducible to percentage efficiency by comparison with the maximum possible lumens per watt, a reasonably well-established constant of photometry.

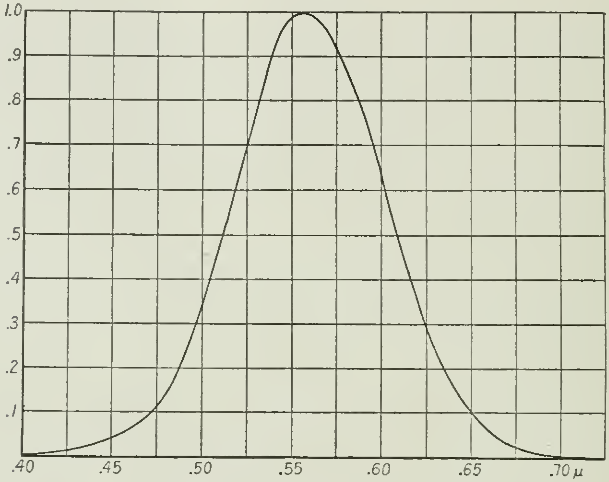
Direct measurements of energy consumption in the glowworm or fire-fly, to say nothing of measurements restricted to the luminous portion, are as yet beyond the range of experiment. We can at best only arrive at an approximate idea of this element of the luminous efficiency by general considerations based on comparison with other organisms. Such a comparative estimate has been made as follows:[4] A man, weighing 75 kilograms, can do about 75 watts work continuously; that is, he has an output of one watt per kilogram. If it can be assumed that energy output in proportion to weight is the same for creatures as diverse as man and the glowworm, we arrive, by using .25 gram as the weight of the glowworm, at the figure .00025 watt as the probable total energy output of the insect. Now about $\frac{1}{10}$ of the glowworms total tissue is devoted to light production, so that we may assume at least $\frac{.00025}{10}$ or .000025 watts expended in light production. The area emitting light is about 10 square millimetres. Hence the work expended per unit of luminous area on those various assumptions is .00025 watts. Using the figure of the last section for the luminous emission, namely, .0144 lumens per square centimetre, we obtain for the total luminous efficiency

$$\frac{.0144}{.00025} = 576 \text{ lumens per watt.}$$

Comparing this with the 640 lumens per watt, which corresponds to 100 per cent. efficiency of light production, we get the striking result that the *total luminous efficiency* of light production by the fire-fly (glowworm) is *90 per cent.*

Exception may be taken to the assumptions made in arriving at this figure, and it cannot claim to be more than a plausible approximation. The calculations do, however, make it seem probable that the luminous efficiency, even if not so high as 90 per cent., is nevertheless many times greater than that of our ordinary light sources, for even if the figure is off by a factor of 3 or 4, or even 10, the efficiency would still be many times the 4 or 5 per cent., which is about the best we now accomplish artificially.

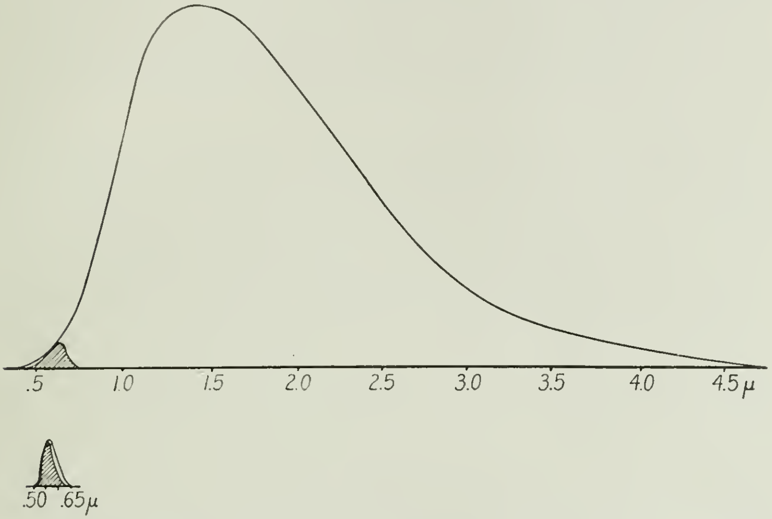
FIG. 7.



Luminous efficiencies of spectral radiations.

High total luminous efficiency implies that the radiational efficiency, and the radiant luminous efficiency, are both high. It would be of interest to verify this conclusion for each of these two efficiencies separately, if possible, and so strengthen the conclusion as to total efficiency. Determination of the radiational efficiency is, in the case of the glowworm or fire-fly, quite beyond our present measuring means. The denominator of the fraction (namely, energy consumed in light production) can only be guessed at by methods such as those of the preceding paragraphs, while the numerator—total radiated energy—is altogether too faint for quantitative measurement by any of the radiometers sensitive to the whole radiant spectrum, such as the thermopile and the bolometer. We can at best merely decide that the energy radiated is enormously less than that from an equally bright light of any other type, or that possibly the luminous portion of the insect is warmer than the non-luminous. But when it comes to the *luminous efficiency of the radiation* we are much better off. In order to measure this it is only necessary to get satisfactory evidence as to *where* in the spectrum the radiation appears, and then to study the spectrum of the radiation at this point by some selective radiometer, which while not sensitive enough for general radiation measurements is adequate for quantitative work in the restricted spectral region. The possibility of doing this of course depends on the radiation proving to be of narrow spectral extent, and on the existence of a suitable selective radiometer. Fortunately both these conditions occur in this problem.

FIG. 8.



Luminous efficiencies of carbon lamp (upper curve) and of fire-fly (lower curve) radiations. Area of outer curves are proportional to total radiation; areas of cross-hatched curves to light-evaluated radiations; the ratio of light-evaluated to total radiation is the luminous efficiency.

In order to find where in the spectrum energy is emitted by the fire-fly, two methods have been used, each of which has the property of integrating repeated small effects over a long interval of time. The first of these is *photography;* the second, is *extinction of phosphorescence.*[5] Photography, with panchromatic plates, covers the range of wave-lengths from .2μ (provided only quartz optical apparatus is used) to .7μ. Extinction of phosphorescence covers the region from .5μ to 1.5μ. The two methods, as shown diagrammatically in Fig. 4, therefore overlap in the visible region, and extend our range of experiment well into the ultra-violet and infra-red.

The photographic experiment to find where the light emitted by the fire-fly lies in the spectrum consisted in placing a series of flashing fire-flies of the species *Photinus Pyralis* over the slit of a small quartz spectrograph. Panchromatic plates were used, the slit of the instrument was quite wide, and exposures continued for an hour. The resulting negative showed *intense action in a narrow band between .5μ and .6μ (Fig. 4) with no trace of action elsewhere.*

Extinction of phosphorescence was utilized as follows: A surface of phosphorescent zinc sulphide was first exposed to an arc light, which induced a phosphorescence which was visible and which could be photographed for several hours. Then by preliminary experiments, it was established that exposure of this surface to light of the wave-length emitted by the fire-fly in the visible spectrum was just about as effective in extinguishing the phosphorescent glow as was the same quantity of radiation anywhere out to 1.5μ. The actual test on the fire-fly then consisted of two experiments; first, its total light was allowed to shine through a small diaphragm and a thin sheet of glass (to stop body heat and moisture) upon the phosphorescent surface. Exposure of only twenty minutes' duration was sufficient to noticeably darken the phosphorescence. Then the experiment was repeated, but this time with a red glass interposed which was opaque to the visible fire-fly light, yet transparent to the infra-red as far as 1.5μ. An exposure of several hours through this glass produced *no trace of action.*

These two experiments showed very conclusively that within the region from the ultra-violet at .2μ to the infra-red at 1.5μ the *radiation of the fire-fly is restricted to a narrow band in the visible spectrum.* While the experiments do not definitely prove that this is the only radiation, it is highly improbable radiations would be emitted outside these spectral regions, for such radiations would be absorbable by the water of the insect's tissues and by the atmosphere. We are therefore justified in proceeding upon the assumption—subject to possible modification by measuring means yet to be developed—that the only radiation of the fire-fly is this narrow band in the visible spectrum.

It now remains for us to study in detail the character of this radiation. How advantageously is it placed in the visible region, for the requirements of vision? To investigate this, use was again made of photography,[6] but this time with a spectrograph of large dispersion, with comparison photographs from which not only exact position but exact distribution of energy could be determined. Fire-flies were held against the spectrograph slit for several hours, one insect after another, as each became exhausted or refused to flash further. Then on the same plate was photographed a line spectrum containing numerous well-known wave-lengths, and also, on this and other plates, a series of spectra of various known intensities, from a light source of known energy distribution. For this latter a carbon incandescent lamp was selected, operated at a definite voltage, and its energy distribution measured through the spectrum as a separate experiment. A photograph of the fire-fly spectrum made in this way is shown in Fig. 5. It will be noted how definitely the light is restricted to a narrow region around $.56\mu$–$.57\mu$, the most luminously efficient part of the spectrum. The next step was to measure the densities of the fire-fly and carbon lamp comparison spectrograms, wave-length by wave-length. This done it was possible by noting the points of coincidence of the fire-fly spectrum densities with one or other of the carbon lamp spectra to establish the relative intensity values of the fire-fly spectrum and the carbon lamp spectrum, and then, by simple proportion, to determine the spectral distribution of energy in the emission of the fire-fly. Fig. 6 shows the result of carrying through this process. For comparison, the energy distribution of the carbon lamp is also shown; that is, as far as the photographic plate and glass prism spectrograph could record it. Its spectrum actually extends many times as far beyond the red, and is still measurable beyond the blue end of the photographed spectrum in the figure.

Before we can find how efficient is the fire-fly radiation, we must know the relative luminous efficiencies of the various radiations. These are shown in Fig. 7 with such a scale of ordinates that the most efficient radiation, at $.56\mu$, is rated 100 per cent. This means that radiation consisting entirely of a monochromatic band of this wave-length would give the greatest possible amount of illuminating power for a given expenditure of energy as radiation. To either side of .56μ the efficiency falls off rapidly, until at and beyond the ends of the visible spectrum it is of course zero. If now we multiply each monochromatic energy emission in Fig. 6 by its efficiency, we get a curve whose area will, in comparison with the unweighted curve, give the luminous efficiency of the radiation. This process is carried through first in Fig. 8 for the "4-watt" carbon incandescent lamp. The ratio of the shaded (light evaluated) to the unshaded (total radiation) curve is .0045; that is, the *luminous efficiency of the radiation from the carbon lamp is less than one-half per cent.* When we apply the same process to the fire-fly radiation Fig. 6, we find *its efficienty to be over 80 per cent.* The exact figure depends upon the species of fire-fly chosen, since the position of the emission band varies somewhat (it is farther toward the blue in the Pennsylvania species whose glowworm was studied, than in the species investigated for the character of the flashing light) and upon the spectral luminous efficiency curve used, *e.g.*, corresponding to high or low illumination. Whether or not any fire-fly has developed absolutely the most efficient light for the use of the *human* eye is not so significant, except from the standpoint of comparative anatomy, as is the fact brought out by shifting the emission curve of Fig. 6, so that its maximum coincides with the maximum of luminous efficiency When this is done it appears that *the fire-fly has developed a type of radiation, which, if placed in the spectrum symmetrically about the wave-length of maximum luminous efficiency, will be of at least 95 per cent. efficiency.*

Summarizing at this point these investigations of the fire-fly's luminous efficiency, we see that whether we study its total or its radiant luminous efficiency the figure arrived at is in excess of 80 per cent. These two efficiencies cannot both be so high unless the *radiational efficiency* is of the same order of magnitude; that is, the process of transforming its bodily energy (input) into radiation (output) must be of the same order of efficiency as in the vacuum incandescent lamp. Thus viewed from every aspect, the conclusion (subject to possible restrictions which have been pointed out) is that the *efficiency* of light production in the fire-fly is comparable with the *inefficiency* of our best processes of artificial light production. In our ordinary illuminants, light is a by-product of a process of heat dissipation; in the fire-fly heat is the by-product of a process of light production.

QUALITY.

It is evident from Fig. 5 that the color of the light given out by the fire-fly is very different from that of an ordinary illuminant, such as daylight or incandescent electric light. It is practically a monochromatic yellow-green. Other colors, being absent from its spectrum, would fail to be visible in objects illuminated by it. The objects in the room imagined in Fig. 3 would all appear as of one color, varying only in intensity. The effect would be like that produced by the old experiment of lighting a room solely by a salt impregnated alcohol flame, only not quite so ghastly, since there is a little orange and blue-green in the light of the fire-fly. In respect to color distribution, it would be rather worse than the mercury arc.

For the purposes of color discrimination or for securing a light of " pleasant " character, the narrow band of emission would have to be widened until it became of the length of the visible spectrum. It is interesting to note that were this done and the energy distribution in the visible spectrum made like that of sunlight, the resultant radiation would still have a luminous efficiency of 40 per cent.; as compared with 14 per cent. for real sunlight.

One advantage of fire-fly light, just as it stands, however, would be in the discrimination of fine detail. Being monochromatic it reduces that diminution of visual resolving power which is caused by the eye's chromatic aberration. *Its color—yellow-green—is just that for which maximum visual acuity is realized.* In this respect it would surpass any artificial light now available.

SUMMARY.

While experimental difficulties do not permit a complete and accurate analysis of all the factors which enter into the evaluation of the fire-fly as an illuminant, it is clear that it does produce a light of sufficient intensity for human use, of a quality which would make it advantageous for many kinds of work. Its efficiency, while less accurately known than its other factors, is undoubtedly exceedingly high, since study of both its total and its radiant luminous efficiency indicate figures of 80 per cent. or better. The same kind of emission, spread through the whole visible spectrum, would still have an efficiency many times greater than any artificial illuminant.

By way of conclusion we may repeat the words of Langley,[7] one of the first to attempt quantitative measurements of the firefly, when he says: "There seems to be no reason why we are forbidden to hope that we may yet discover a method (since such a one certainly exists and is in use on a small scale) of obtaining an enormously greater result than we now do from our present ordinary means for producing light." It has been the object in this paper to indicate the size of Langley's "enormously greater result."

REFERENCES.

[1] W. H. Pickering: *Nature*, **97**, p. 180, April 27, 1916.

[2] Ives and Jordan: *Lighting Journal*, Feb., 1913, p. 47.

[3] Selected from "Illuminating Engineering Practice," McGraw Hill, 1917, p. 61.

[4] McDermott and Ives: *Lighting Journal*, March, 1914, p. 61. (The result there published is in error by the factor π.)

[5] Ives: *Physical Review*, Dec., 1910, p. 637.

[6] Ives and Coblentz: *Trans. Illuminating Eng. Soc.*, Oct., 1909, p. 675.

[7] Langley and Very *Smithsonian Misc. Coll.*, n. 1258.

A New Method of Using X-Rays in Crystal Analysis. G. L. CLARKE and WILLIAM DUANE. (*Proc. Nat. Acad. Sciences*, May, 1922.)—An essential feature of this method is the use of a continuous spectrum of X-rays and not merely a line spectrum. The crystal, either powdered or intact, is put at the centre of an X-ray spectrometer which has an ionization chamber. It reflects at certain positions a considerable part of the incident beam of X-rays into the chamber. When a set of parallel planes of the crystal comes into a definite direction, the reflected beam is of maximum strength. The crystal is turned and the strength of the currents caused in the ionization chamber by the reflected beam is measured from each position. From the angles between the positions for which the ionization reaches maxima it is possible to infer the angles between the crystal planes producing the reflection. Great accuracy in the measurement of crystal angles is obtained by this method. When a crystal of KI was investigated the angles between maxima came out 44.96°, 18.37° and 26.52°, "which correspond very closely with the angles between some of the principal planes in a cubic lattice, namely 45°, 18.43° and 26.57°."

It is very interesting to note the name of a descendant of Benjamin Franklin at the head of article after article recording advances in physics.

G. F. S.

THE EFFECT OF ABSORBED GAS ON THE CONDUCTIVITY OF GLASS.*

BY

V. BUSH, Eng.D., and L. H. CONNELL, S.B.

Massachusetts Institute of Technology.

THIS paper presents the results of an investigation on the electrical properties of glass carried on during the past two years in the Research Laboratories, Department of Electrical Engineering, Massachusetts Institute of Technology. Briefly, these results show that gases, in particular water vapor, penetrate throughout the volume of glass and quartz, and radically affect their volume conductivity.

Langmuir[1] has measured the amount of gas removed from glass by heating in vacuum. He found this gas to consist principally of water vapor and also showed that the total amount liberated varied with temperature up to the softening point of the glass. On the assumption of absorption, the amount of water obtained corresponded, for a representative specimen, to a surface layer 55 molecules deep. Some penetration is hence evident; and Langmuir concludes that a solution of the water in the glass takes place. The results of a number of other investigations[2] indicate a similar conclusion. The present investigation was undertaken to determine whether penetration occurred throughout the volume, and whether some light could not be thrown upon the electrical conductivity of vitreous materials.

The specimens on which conductivity measurements were made were prepared as shown in Fig. 1. A tube of the material to be tested was closed at one end. Electrodes were placed inside and outside by copper plating. Care was taken that these should adhere firmly to the glass. Small parts of the outer electrode in numerous places were removed to render bare the glass underneath. The specimen was then mounted, as shown, in a tube which could be exhausted. Three guard rings were plated on.

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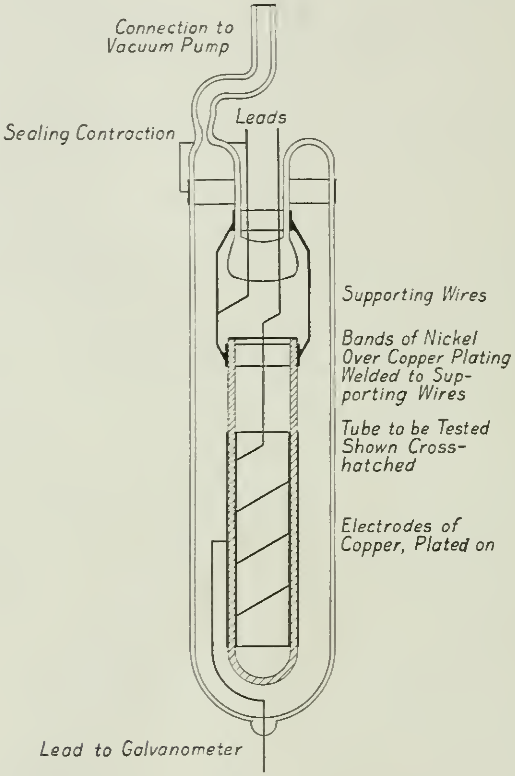
* Communicated by Dr. V. Bush.

[1] *J. A. Chem. Soc.*, **38**, 2283 (1916); *Trans. A.I.E.E.*, **32**, 1921 (1913).

[2] Dushman, G. E., *Review*, **24**, 246 (1921), gives an excellent summary of this previous work.

These rings were so placed and connected as to prevent current passing through the measuring instrument except that which flows from outer to inner electrode through the body of the specimen. The guard ring on the specimen itself was placed close to the outer electrode in order that the measurement of volume conductivity might not be grossly affected by changes in the effective area of the electrodes due to variations in surface conductivity.

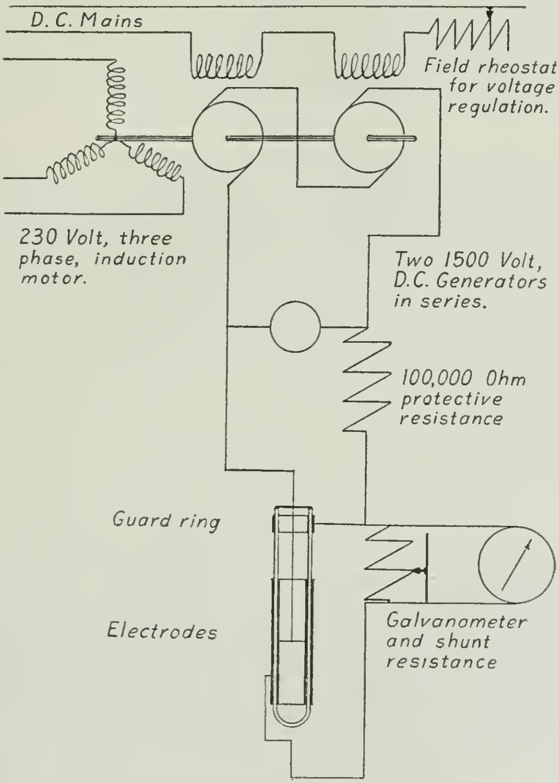
FIG. 1.


Connection to Vacuum Pump
Leads
Sealing Contraction
Supporting Wires
Bands of Nickel Over Copper Plating Welded to Supporting Wires
Tube to be Tested Shown Cross-hatched
Electrodes of Copper, Plated on
Lead to Galvanometer

The diagram of connections is shown in Fig. 2. A generator was used capable of delivering 3000 volts constant potential. The galvanometer used was calibrated from time to time, and gave an average constant of 1.722×10^{-9} amperes per mm. deflection, which did not vary enough to require special attention.

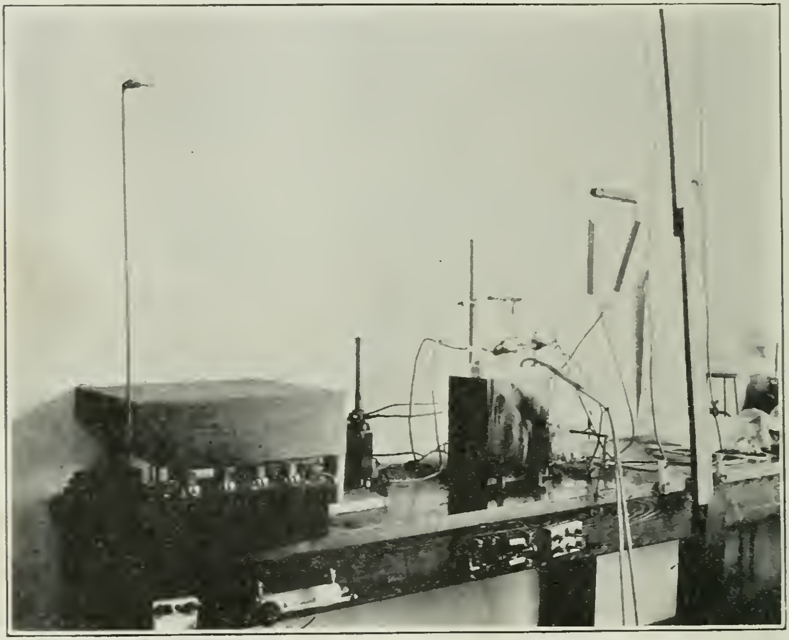
The layout of apparatus was as shown in Fig. 3. Insulation was obtained by suspending parts at high potential by silk threads from glass rods. This insulation was tested from time to time by breaking the connection to the outer electrode immediately adjacent to the tube, taking the shunt off the galvanometer, and applying full voltage. A deflection under these conditions greater than 3 mm. was not tolerated. As the measurements were carried on with a deflection of approximately 100 mm., and a shunt ratio of about 10:1, it is believed that ample insulation was provided.

FIG. 2.


D. C. Mains
Field rheostat for voltage regulation.
230 Volt, three phase, induction motor.
Two 1500 Volt, D.C. Generators in series.
100,000 Ohm protective resistance
Guard ring
Electrodes
Galvanometer and shunt resistance

Constant temperature on the sample was maintained by immersing the containing tube in oil to within one centimetre of the top, thus leaving the lead to the inner electrode entirely in air. The temperature of the oil was maintained constant at 25.00 ± .05 degrees Centigrade by a heater and automatic control. Preliminary curves of resistivity against temperature for representative specimeans of glass had a slope of approximately 10^{10} ohms per centimetre cube per degree Centigrade at the temperature of 25° C. chosen for the measurements. For the preliminary work we are indebted to Mr. F. C. Tsu and S. L. Yang. The measured values of resistivity at 25° C. were always above 10^{11} ohms per centimetre cube, and as temperature was held well within .1 degree, the error due to temperature change was probably always less than 1 per cent. The specimens were kept in the constant temperature bath for half an hour before taking readings, to make sure the specimen itself had reached the desired temperature. The effectiveness of the guard rings was investigated on typical samples by transferring the galvanometer to the guard ring lead. The greatest current measured in this lead was about 20 per cent. of the current flowing to the outer electrode. Surface conduction on the specimen results in increasing the apparent area of the electrodes, but the error from this source may be expected to be less than 10 per cent. When, during a measurement with the galvanometer connected as in Fig. 2, the lead to the guard rings was

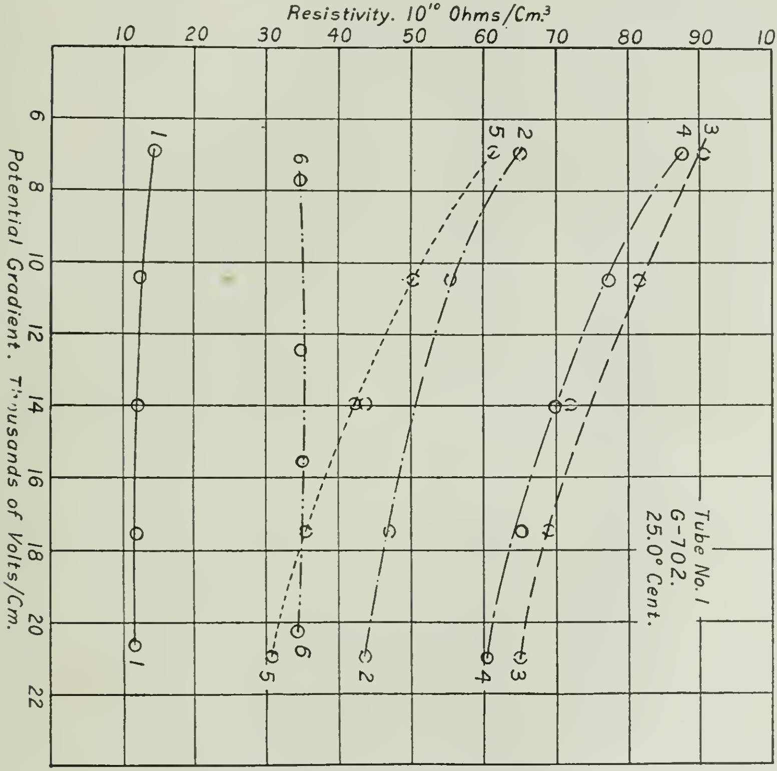
Fig. 3.



opened, the current flowing through the galvanometer usually increased about 10 per cent. This again indicates that the stray current error is reasonably small.

With each specimen the following procedure was carried out as far as possible:

FIG. 4.



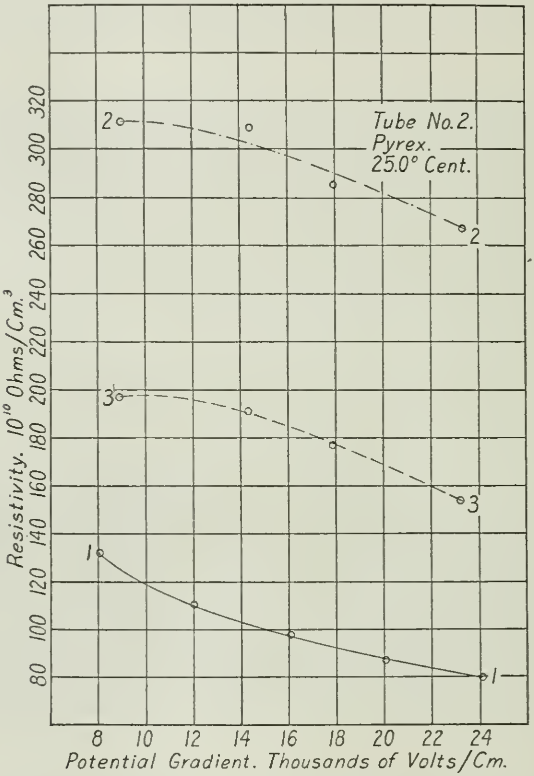
1. The specimen, mounted in its containing tube, was washed in ether and dried by warm air. It was then brought to constant temperature and its resistance measured for various values of applied potential.

2. The containing tube was then exhausted with a Langmuir pump and heated to 350° C. until no further gas was evolved. It was then sealed off the pump. After cooling, it was brought to constant temperature, and resistance measurements were repeated for the same values of applied potential as were used previously.

3. The seal in the outer tube was now cracked to allow air to enter; and another curve was taken as soon as possible. This was intended to detect any error which might be present due to gaseous conduction in a poor vacuum.

4. After the lapse of a few hours or days, the measurements of resistance were again made.

Fig. 5.



The results on the first specimen are shown in Table I. This was a piece of G-702 Corning glass. The values given in this table are plotted in Fig. 4. Curve 1 applies to the untreated tube. During exhaustion the outer tube cracked when the temperature reached 300° C., but a curve was immediately taken and is shown at 2. The outer tube was repaired and exhaustion at 350° C. was then completed. Curve 3 was obtained immediately after this exhaustion. The seal was then cracked to admit air. Curve 4

TABLE I.

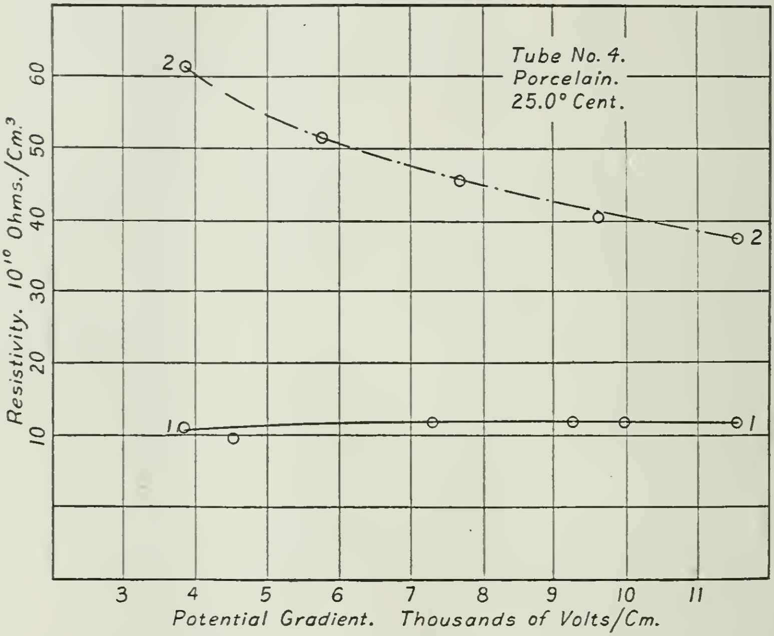
Tube No. 1 *G702* 25.0° C.

Inside Diameter, 1.58 cm.
Outside Diameter, 1.87 cm.
Length of Electrodes, 10.0 cm.

	Impressed Voltage Volts	Resistance Ohms	Potential Gradient Volts/cm.	Resistivity Ohms/cm.^{3}
(1)	2950	314×10^6	20600	11.90×10^{10}
	2510	317	17520	12.00
	2005	322	14000	12.20
	1500	333	10460	12.62
	1000	337	6980	14.30
(2)	3000	1150×10^6	20940	43.6×10^{10}
	2500	1240	17440	47.0
	2000	1160	13960	43.9
	1500	1470	10460	55.7
	1000	1720	6980	65.1
(3)	3000	1720	20940	65.1×10^{10}
	2500	1820	17440	69.0
	2000	1900	13960	72.0
	1500	2160	10460	81.8
	1000	2390	6980	90.5
(4)	3000	1600	20940	60.6
	2500	1720	17440	65.1
	2000	1845	13960	70.0
	1500	2040	10460	77.4
	1000	2310	6980	87.5
(5)	3000	812×10^{-6}	20940	30.8×10^{10}
	2500	923	17440	35.4
	2000	1110	13960	42.1
	1500	1330	10460	50.4
	1000	1620	6980	61.4
(6)	2890	902×10^6	20200	34.2×10^{10}
	2670	827	18640	31.3
	2450	995	17100	37.7
	1780	900	12420	34.1
	1335	596	8320	22.6
	2890	908×10^6	20200	34.4×10^{10}
	2225	923	15520	35.0
	1780	920	12420	34.8
	1112	914	7760	34.6

was taken about eighteen hours later. After three days, the results were as shown in Curve 5. A measurement at 3000 volts, taken from time to time during the next few weeks, showed the values given in Curve 5 to remain substantially constant.

Fig. 6.



As a further experiment, this tube was then placed in an iron pipe and subjected to three pounds steam pressure for two days. The outer tube cracked during this treatment, so that the specimen itself was placed in contact with the oil to obtain the values shown in Curve 6. This last curve is probably unreliable. It indicates interesting possibilities which should be studied.

It will be noted that the measured values of volume resistivity were increased in the ratio of approximately 6 : 1 by the removal of the water vapor and other gas from the glass. Some of this change is no doubt due to an alteration in surface conductivity as noted above; but only a relatively small part can be accounted for in this manner. There is evidently a large change in the volume conductivity when heated in vacuum. Upon subsequent exposure to the air the resistivity decreased slowly, but did not reach its original value. These results suggest interesting scientific and technical possibilities.

Other specimens were similarly tested. In Fig. 5 are shown the results for "Pyrex." Curve 1 was taken on the fresh specimen, Curve 2 after exhaustion at 360° C., and Curve 3 after the specimen had been opened to the atmosphere for three days. The tube was then broken accidentally.

FIG. 7.

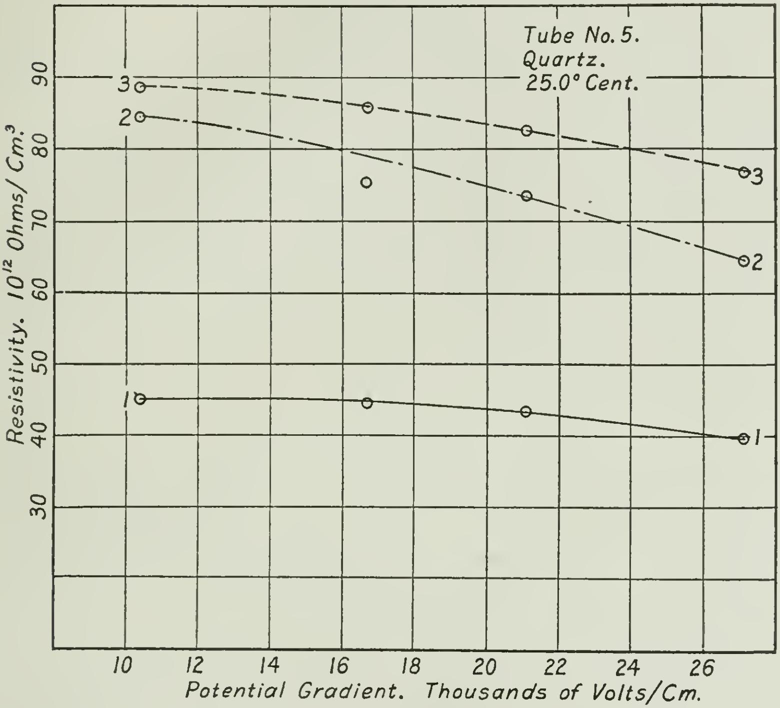


Fig. 6 gives the results with a specimen of porcelain. Curve 1 applies to the raw specimen, and Curve 2 after exhaustion at 350° C. This specimen also met with an accident.

Fig. 7 was taken with fused quartz. The precision of the results on quartz was less than on glass as the resistivities measured were much higher. Curve 1 was taken on the new specimen, Curve 2 after exhaustion at 350° C., and Curve 3 after subsequent exposure to the air for two days. Several times during the next two months single points were taken, and were always found to lie between Curves 2 and 3. Apparently the resistivity of quartz does not decrease rapidly on exposure to air after vacuum treatment.

As a further check on results the dielectric loss in one specimen was measured at 1000 cycles per second before and after vacuum treatment. It was found to decrease by about 20 per cent. This has not as yet been carefully studied.

It is believed that the above measurements show definitely that gases penetrate throughout the volume of glass or quartz, and thus affect its electrical conductivity and probably other properties. A considerable improvement in insulating value or dielectric loss can be obtained by vacuum treatment and part of this improvement is apparently permanent. Some penetration of moisture into the body of the glass occurs from the atmosphere at ordinary temperatures.

We realize that the above is only a beginning, and propose to continue the investigation.

Massachusetts Institute of Technology,
April 17, 1922.

The European Commercial: A New "World" Newspaper.—The following from *The Chemical News* will be interesting to American business men. An important step in the rehabilitation of European trade, and indeed the trade of the entire world, will be the publication, under British auspices, in Vienna, in a few weeks' time, of a new periodical, claiming to possess " an authority and a status of an altogether exceptional character."

Under the imposing title of *The European Commercial,* this ambitious venture has the approval and will enjoy the active support of most of the European Governments, will be accorded special facilities for the collection of authoritative news, and will circulate through Government circles. With a staff of commercial experts selected from the leading markets of the world, and with local editors and correspondents in every important city in Europe, it will at once assume, so its promoters claim, an unchallengable position as a real World Newspaper.

Although Vienna has been selected as the publishing centre, on account of its hospitality, its cosmopolitan character, and its favorable situation, *The European Commercial* will be printed in English. It will conduct no propaganda, its mission being simply to bring business men together and to give them facts and figures. To maintain strict impartiality among the various countries, the advertising space will be rigidly rationed.

H. L.

NOTES FROM THE U. S. BUREAU OF STANDARDS.*

DURABILITY OF SOLE LEATHER FILLED WITH SULPHITE CELLULOSE EXTRACT.[1]

By R. C. Bowker.

[ABSTRACT.]

THIS paper describes the preparation of four lots of leather used to determine the comparative durability of sole leather filled with sulphite cellulose extract and sole leather filled with ordinary vegetable tanning materials such as chestnut wood and quebracho extracts. Several hides were used in the preparation of each lot, and alternate sides were filled with the sulphite cellulose extract. Each pair of soles contained one sole prepared by each method, both of which were cut from the same hide and from similar locations.

The results of actual service tests are presented which show that the average wear of the leather filled with sulphite cellulose extract was 9.08 days per unit thickness and of the ordinary leather 9.06 days.

Complete chemical analyses of both the new and worn soles are also given.

The general conclusions are that there is no difference in the two leathers as reflected by the chemical analyses; that sole leather filled with sulphite cellulose extract is as durable as leather filled with chestnut wood and quebracho extracts, and that the former could well be used in place of the latter materials, thereby conserving them for the actual tanning of leather for which they are more suitable than sulphite cellulose extract.

SOURCES OF ELEMENTARY RADIO INFORMATION.[2]

[ABSTRACT.]

A VERY considerable number of persons are interested in the operation of radio stations, who are not directly concerned with

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* Communicated by the Director.

[1] Technologic Paper No. 215.

[2] Circular No. 122.

the operation of either Government or regular commercial radio stations. Some are interested in maintaining a private system of radio communication over comparatively short distances. Many are interested in radio because it offers a very fascinating experimental field. Different kinds of useful information, such as weather reports, market reports, time signals, and music, and other entertainment are transmitted daily by radio, and are received by many persons in all parts of the United States.

The recent developments in radio communication have been so rapid that much important radio information has not yet been collected in books, but must be sought in periodicals and other sources. A number of important books have appeared very recently and are not yet generally known. The Bureau of Standards is constantly receiving requests for radio information. The same information is called for by many of the inquiries received, and in order to facilitate the answering of such inquiries, this Circular has been prepared. This Circular gives information concerning radio periodicals, Government radio publications issued by various bureaus, radio books, issued by various publishers, radio laws and regulations, call letters, and safety precautions to be observed at radio stations, and answers a few of the most usual elementary questions concerning radio communication which are asked by the novice.

The periodicals devoted primarily to radio communication which are now available may be divided into three general classes. About half a dozen periodicals which have been in existence for two years or more are devoted to the interests of the radio amateur, that is, to the interests of the person who wishes to make radio experiments and to develop his own apparatus and often to transmit and receive radio telegraph messages over long distances, as from the Atlantic Coast to the Pacific Coast. There are two or three periodicals devoted to radio which are intended primarily for the professional engineer and scientist and contain papers which are usually of advanced technical interest. In addition, there is a third class which has very recently come into existence which is intended primarily for the radio novice, that is, the person who has only comparatively little familiarity with electrical and radio apparatus, but wishes to receive certain information and entertainment transmitted by radio, usually by radio telephony. Prior to 1921, there were only a comparatively few persons interested in radio from the novice point of view. The recent development of broadcasting by radio telephony has caused a very large number of persons to install radio receiving equipment. In the course of three months, seven new periodicals, intended for the novice, have been established, and it is expected that others will appear shortly.

The United States Department of Commerce, Bureau of Navigation, issues a monthly periodical called the *Radio Service Bulletin,* which will be found of interest to every person engaged in radio communication. The subscription price is twenty-five cents per year, and orders may be placed with the Superintendent of Documents, Government Printing Office, Washington, D. C.

The Bureau of Standards has prepared an elementary textbook, Signal Corps Radio Communication Pamphlet No. 40, "The Principles Underlying Radio Communication." This book contains 600 pages and more than 300 illustrations, durably bound in fabrikoid. Every person interested in radio communication will find this book useful. A copy can be purchased for one dollar from the Superintendent of Documents, Government Printing Office, Washington, D. C.

The Bureau of Standards has prepared a considerable number of professional Scientific Papers on radio subjects. These papers are listed in this Circular.

Information is given regarding the safety precautions which should be observed in radio installations. The rapid development of the radio art has required a revision of the rules for radio installations made by the National Board of Fire Underwriters. Sources of information are given from which particulars may be obtained about new rules proposed by the Underwriters.

The United States radio laws provide that in order to operate a transmitting station, both a *station* license and an *operator* license must be secured. In the United States, no station license is required for a station used only for reception. This Circular gives information regarding the granting of both station licenses and operator licenses, including the various grades of licenses of each kind which are granted. Information is also given regarding the Canadian radio laws, which differ considerably from those in force in the United States.

This Circular also gives information regarding call letters assigned to Government, commercial and amateur radio stations in the United States. Separate call books are sold by the Superintendent of Documents, Government Printing Office, Washington, D. C., for amateur stations and commercial and Government stations, and information is given as to the proper method of securing each of these call books.

NOTES ON STANDARD WAVE-LENGTHS SPECTROGRAPHS, AND SPECTRUM TUBES.[3]

By W. T. Meggars and Kelvin Burns.

[ABSTRACT.]

I. *Standard Wave-lengths in the Cadmium Spectrum.*—The wave-lengths of thirteen lines in the spectrum of tubes containing cadmium vapor at low pressure are measured relative to the primary standard (6438.4696A) by means of the Fabry and Perot étalon interferometer. The adopted values in International Angstrom units are as follows:

2980.6216
3080.827
3133.167
3252.5248
3403.6529
3466.2010
3467.6559
3610.5098
3612.8748
4662.3525
4678.1504
4799.9139
5085.8230
6438.4696

The probable error in most of these values is less than 0.001 A, and evidence that the wave-lengths derived from spectrum tubes are reproducible is presented. Constant frequency differences which define the separation of subordinate series limits are established:

$$2p_1 - 2p_2 = 1170.866$$
$$2p_2 - 2p_3 = 542.104$$

II. *A Quartz Rock Salt Spectrograph.*—An instrument whose optical parts consist of quartz and rock salt is described. This spectrograph was designed for photography of interference phenomena in the ultra-violet, but is also serviceable in the visible spectrum and has certain advantages (larger dispersion, flatter field, partial achromatism) over the usual types of quartz spectrographs for investigating the shorter waves.

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[3] Scientific Papers, No. 441.

III. *A Stigmatic Concave Grating Mounting.*—The Wadsworth mounting in which the slit is, in effect, placed at infinity with the aid of an auxiliary mirror, thus filling the concave grating with parallel light, gives spectral images which are practically free from astigmatism. This permits the use of diaphragms in front of the slit for the photography of comparison spectra in juxtaposition, and makes it possible to study the spectra of interferences, or of localized parts of sources whose images are focussed on the slit. Compared with the Rowland type of mounting, it requires only about one-fourth the space, and although the dispersion is reduced to about half, the intensities of the spectra are increased more than four-fold. The characteristics are outlined and detailed drawings of the apparatus are reproduced.

IV. *The Preparation of Spectrum Tubes.*—Instructions and suggestions are given for the preparation of Plücker tubes commonly required for optical demonstration, testing and research. The remarks apply especially to tubes containing hydrogen, nitrogen, oxygen, helium, neon, and argon. It is sometimes inconvenient or impossible to purchase such tubes ready made, and it is pointed out that laboratories possessing a good vacuum pump and a glass blower can easily prepare their own tubes.

DURABILITY OF CEMENT DRAIN TILE AND CONCRETE IN ALKALI SOILS; THIRD PROGRESS REPORT (1919–20).[4]

By G. M. Williams.

[ABSTRACT.]

THE third progress report on the investigation of the durability of cement drain tile and concrete exposed to alkali soils and waters gives an account of the condition in 1919 and 1920 of experimental drains laid in western alkali districts in 1913, and of large concrete blocks similarly exposed in 1915. Both drain tile and concrete blocks were made up in sufficient quantity and variety to be representative of all qualities, and were installed in typical alkali sections of the arid belt from New Mexico to Montana.

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[4] Technologic Paper No. 214.

With reference to drain tile the following tentative conclusions have been drawn:

1. The use of cement drain tile in soils where sulphates occur in considerable quantities is hazardous. In certain localities the best quality of tile disintegrated within six years.

2. Porous or permeable tile, made from lean or dry mixtures, are subject to disintegration in sulphate waters of relatively low concentrations.

3. Disintegration of mortar or concrete in sulphate waters may be due in part to physical forces arising from crystallization of salts in the pores, but it is primarily due to chemical attack upon the cement.

4. In the best quality of tile the outer skin may sometimes remain apparently unaffected, at the same time allowing the alkali water to pass through and attack the mass underneath.

5. In tile of given quality exposed to sulphate waters, the disintegrating effect seems to vary with the concentration.

6. Tile made-by-hand or with the packer-head type of machine, and of sufficiently dry consistency to permit immediate removal of the molds, are less resistant to alkali action than tile of a wetter consistency which requires their retention in the molds for a period of hours.

7. Tile cured with steam seem to be no more resistant to alkali attack than those cured by systematic sprinkling. Tar and cement grout coatings were not effective in protecting the tile.

8. If cement drain tile are to be used in soils or waters containing more than 0.1 per cent. of sulphates, careful consideration should be given to sub-surface conditions, the quality of tile to be used, etc.

9. Quality of cement drain tile can best be measured by permeability tests. There appears to be little definite relation between permeability and the related factors of porosity, absorption, and density.

With regard to concrete the following tentative conclusions have been drawn:

1. Materials of good quality and proper workmanship are of great importance in the fabrication of concrete exposed to alkali soils and waters.

2. Surface action on concrete blocks of good quality after one year's exposure has in most cases been progressive.

3. The extent and rapidity of disintegration depends upon concentration of soluble sulphates.

4. Disintegration of concrete blocks containing reinforcing rods has in some cases been aided by corrosion of the rods and consequent splitting of the concrete.

5. Concrete structures exposed to alkali waters should be given all possible protection by drainage.

6. Concrete of the best quality will disintegrate if exposed to sufficiently high concentrations of alkali, such as were encountered in some of the locations where the test blocks were installed.

7. So far as the tests indicate, the resistance to alkali action of mass concrete, made of the same aggregates and exposed to the same concentrations, varies with the cement content or richness of mix. This again seems to indicate that strength and permeability, rather than absorption, are the governing factors in determining the quality and durability of concrete under alkali exposure.

The paper carries two appendices, one containing a summary of the absorption tests on samples of all types of drain tile used in the investigation, and the other a discussion of the occurrence of soluble salts in the soil and their action on cement and concrete.

POWER LOSSES IN AUTOMOBILE TIRES.[5]

By W. L. Holt and P. L. Wormeley.

[ABSTRACT.]

THE Bureau of Standards has undertaken a general investigation of automobile tires and inner tubes, and in connection with this work a rather comprehensive program has been laid out for dynamometer tests, to study among other things the power losses or energy dissipated into heat in tires operated under different conditions of axle load, inflation pressure, speed, temperature, and tractive effort. Preliminary tests have been made to determine the influence of these factors, which, aside from matters of design, are the principal items affecting the power loss in a tire. A continuation of the work will involve problems of design and construction, the influence of "over-size" tires and of "cord tires" on power losses, mileage, and general efficiency of operation. An

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[5] Technologic Paper No. 213.

investigation will be made of inflation pressures as affecting the efficiency and economy of tire operation. Tests will be made to determine the effects of tire fillers, shields, puncture proof tubes, etc., and the properties of cushion tires will be studied.

The equipment consists of two Sprague electrical absorption dynamometers having a capacity of 20 horsepower at 600 r.p.m. and 10 horsepower at 150 r.p.m. One dynamometer is operated as a motor carrying on its shaft a wheel and the tire to be tested. The other dynamometer is operated as a generator carrying on its shaft a smooth straight face iron drum 40 inches in diameter. The motor is mounted on a movable carriage, the arrangement being such that by the application of weights to a bell crank lever the tire is forced against the drum with a pressure corresponding to the desired axle load. In this way the tire and drum constitute a friction drive by means of which the motor drives the generator. The field pole frame of each dynamometer is supported in ball bearings concentric with the armature shaft, and when in operation the magnetic drag or torque is measured on a Fairbanks scale. Each dynamometer is provided with a centrifugal tachometer which indicates the approximate speed in r.p.m. and with a mechanical revolution counter operated by a magnetic clutch. The revolution counters are so designed that they may be read to the nearest one-tenth revolution of the tire or drum. The control panel is completely equipped for regulating the motor speed and generator load. Resistance grids are provided for absorbing the power generated. A switch is provided for operating simultaneously a stop watch and the revolution counters.

METHOD OF DETERMINING POWER LOSS

The distance from centre of shaft to knife edge on each element is 15.756 inches, so that the power output of the motor and the power input of the generator are computed by the formulas

$$HP_1 = \frac{T_1N_1}{4000} \qquad (1),$$

and

$$HP_2 = \frac{T_2N_2}{4000} \qquad (2).$$

Where T_1 = scale reading of motor element in pounds (corrected for windage).

T_2 = scale reading of generator element in pounds (corrected for windage).

N_1 = Revolutions per minute of tire.
N_2 = Revolutions per minute of drum.

The power loss in a tire is given by the equation:

$$HP_1 - HP_3 = \frac{T_1N_1 - T_2N_2}{4000} \text{ (horsepower)} \quad \ldots\ldots\ldots\ldots\ldots\ldots (3).$$

This loss is due partly to deformation of the tire, and partly to slip. The part due to deformation represents heat developed in the tire, and the part due to slip represents heat developed at the surface of contact between tire and drum.

Perception of the Direction of Sounds and Some Technical Applications. W. KUNZE. (*Physikal. Zeit.*, December 1, 1921.)—Our ability to determine the direction from which sounds come depends upon the simultaneous use of both ears. At the two ears there are possible differences in three physical features of sounds arriving from the same source, *viz*—intensity, phase and instant of reception. The two former differences have usually been called on to furnish an explanation of the perception of direction, but the attempt has not been successful. On the other hand, the explanation founded on the interval between the arrival of the sound at the two ears and published by Hornbostel and Wertheimer in 1915 is congruent with the facts. These men experimented with noises, instead of with tones, as was done by Rayleigh and his school.

If the interval is zero, then the sound is perceived as directly in front or behind, that is, in the median plane of the head. The same judgment is formed for time intervals up to .00003 sec., the time required for the sound wave to traverse about one centimetre in air. As the interval grows beyond .00003 sec. the sound is perceived to come more and more from the side until it seems in the line joining the ears when the interval is .0006 sec. or over. Of course if the interval is made too great, the two sounds will be heard as separate impressions In .0006 sec. the wave travels about 21 centimetres in air, and it might be supposed that this is the distance from one ear to the other or, perhaps, half the perimeter of the head, but this is not the case. The 21 centimetres seems to be an empirical constant of unknown significance. This constant should be larger for an elephant than for man, and the animal ought to be able to determine direction more precisely than man. It is, however, possible to use a longer base for sound observations by setting two artificial receivers more than 21 centimetres apart and connecting them to the two ears by tubes of equal length. Suppose that with the unaided ear the interval is .00002 sec. The inference will be drawn that the sound originates in the median plane. Then substitute the receivers in the line joining the ears, one on each side of the head and the distance from ear to receiver being the same on both sides. With this arrangement the interval between the instants of arrival of the sound waves at the receivers will, with a sufficiently long base, surpass .00003 and the direction will not seem in the median plane but at one side. It thus becomes possible to judge directions with greater accuracy. This is not a fine spun theory merely, for the Germans put it into use during the war.

When the sound seems to originate in the median plane, the ear can note departures from this plane of about one degree, while well at the side a divergence of ten times as much is the smallest noticeable. When artificial receivers, such as microphones, are used to locate the sound source, it is not necessary to move the head of the observer. The line joining the instruments may be swung around or they may be maintained at rest while the length of path from ear to instrument is varied. There is an ambiguity in such measurements, since the same interval arises from sounds coming from the same direction either in front or behind. This is removed by swinging the arrangement through a right angle.

As sound travels 4.3 times as fast in water as in air, for the same accuracy of judgment the base in the liquid should be 4.3×21 centimetres long. The Hun submarines used such an arrangement to aid them in work.

Suggestions are made of applications of the great sensitiveness of the ear in perceiving direction. At the distant ends of two tubes of equal length are two telephone receivers actuated by the same microphone. Each tube leads to an ear. One tube has air, the other a gas in which the speed of sound is to be measured. The two sound waves, starting at the same time, will reach the ears at different times. By some compensatory method it can be made to appear that there is one sound in the median plane. The interval and, indirectly, the speed can be obtained from measurements of the compensation employed. Another application that has given good results in water is this. The problem is to measure the distance between two points. At each point place a sound receiver and join these to the ears by tubes of equal length. Let the source of sound give a tone of variable frequency, and for simplicity let it be somewhere on the line connecting the receivers. When the frequency is increased gradually, there will come a time when the ear perceives the sound in the median plane. In general this is at the instant when an impulse reaches one ear at the same time that the next following impulse arrives at the other ear. The distance from one point to the other equals the velocity of sound in the medium divided by the frequency of the source, that is by the number of impulses per second.

G. F. S.

NOTES FROM THE LABORATORY OF APPLIED SCIENCE, NELA RESEARCH LABORATORIES.*

AN INTERFERENCE THERMOMETER AND DILATOMETER COMBINED.

By M. Luckiesh, Director, L. L. Holladay, Physicist, and
R. H. Sinden, Assistant.

[ABSTRACT.]

It is a simple interference method of measuring a change of temperature and the corresponding expansion of three similar test specimens which are arranged symmetrically between two fused quartz plates. When the plates are illuminated normally with monochromatic light one set of interference fringes is produced by light reflected between the upper and lower surfaces of the upper quartz plate. After the quartz plate has been calibrated, the number of fringes that shift past a reference mark on the lower surface of the upper quartz plate provides a measure of the change in temperature of the quartz plate. In order to calibrate the quartz plate as a thermometer, a standardized thermocouple may be used to measure the change of temperature of the furnace and quartz plate. By changing the temperature of the furnace very slowly the lag of temperature between the thermocouple and the quartz plate may be reduced to a minimum. By making the test first with increasing temperature and then with decreasing temperature the total lag may be definitely determined.

The calibration may be checked by making an expansion test upon some substance whose expansion coefficient is accurately known. This may be done by the usual interferometer method by the addition of a second quartz plate. The specimens are placed between the two plates and a second set fringes is produced by the interference of light reflected between the lower surface of the upper quartz plate and the upper surface of the lower quartz plate. The number of these fringes that shift pass the reference mark gives a measure of the expansion of the specimens.

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* Communicated by the Director.

THE COST OF DAYLIGHT.[1]

By M. Luckiesh and L. L. Holladay.

[ABSTRACT.]

DETAILED estimates have been made of the initial and annual costs of natural and artificial lighting. The initial net cost of equipment for natural lighting consists of the difference in cost of the building with and without windows (or skylights), the cost of real estate occupied by the light courts, and the cost of the extra heating system to supply the difference in heat losses from the windows and skylights and the wall replaced by the glass areas. The annual cost of natural lighting consists of interest upon the initial net cost, depreciation, cost of repairs, washing and extra fuel.

The initial cost of equipment for electric lighting consists of the cost of wiring, fixtures and portables; and its annual cost consists of interest upon the initial investment, depreciation, repairs, lamp renewals and electric energy.

In conclusion, it may be stated that the initial net cost of equipment for natural lighting is, for dwellings from 110 to 225 per cent. of the initial cost of the electric lighting; for apartments and hotels from 100 to 140 per cent.; for offices about 160 per cent.; and for art galleries 80 to 180 per cent. The annual cost of natural lighting is, for dwellings from 95 to 125 per cent. of the electric lighting; for apartments, hotels and offices, where electric lighting is freely used at all hours of the day, from 50 to 100 per cent.; and for art galleries about 135 per cent. of the electric lighting. The cost of artificial lighting used in the daytime to reinforce daylight has not been charged to natural lighting in the foregoing estimates. If this had been done the cost of daylight would have been appreciably greater in some cases.

SOME OPTICAL PROPERTIES OF RHODAMIN B.[2]

By A. Poritsky.

[ABSTRACT.]

THE paper comprises a study of various optical properties of solutions of fluorescent Rhodamin B in alcohol. It was found that

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[1] To appear in the *Trans. I. E. S.*

[2] This work, begun in the Physical Laboratory of Cornell University, is to appear in the *Phys. Rev.*

within the studied region Beers' law and Lamberts' law of absorption are obeyed.

The wave-length where maximum energy in the fluorescence occurs shifts towards the infra-visible as the concentration is increased from 1 to 100; and remains there (583 mμ) for all further concentrations up to 10,000.

Previous exposure of concentrated solutions to intense light and heat shifts this wave-length toward the ultra-visible.

A film of dry rhodamin shows metallic reflection with one maximum fluorescence for concentrated solutions, and another lesser maximum at 540 mμ. The minimum at 550 mμ coincides with the maximum of absorption.

THE SCOPE OF SPECTROSCOPY.[3]

By Enoch Karrer.

[ABSTRACT.]

A GENERAL survey is given of some recent discoveries in spectroscopy and their application. It is pointed out how with the recent explorations in the extreme ultra-violet and the Röntgen regions, the electromagnetic spectrum has been almost completely mapped out in the sense that either the wave-lengths have been isolated, measured directly or indirectly, or some property of matter has been studied in reference to the radiation. There remains a small portion of the spectrum between the longest infra-red waves and the shortest Hertz wireless waves in which neither wave-length nor properties of bodies have been studied. No limit has been found to the shortness of X-rays and gamma rays.[4]

One of the most important advances recently made is the formulation between wave-length and voltage required to arouse radiation (*viz.,* λ V 12345). There are critical values of voltage at which radiation of certain wave-length appears without ionization, and others with ionization. Other ideas touched upon are, quantitative analysis by spectroscopy; constancy of spectra; number of spectral lines given by the elements; graphical representation of the atom.

From the standpoint of illuminating engineering the spectrum may be divided into three parts: the visible, the ultra-visible and the infra-visible.

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[3] To appear in *Gen. Elec. Rev.,* July, 1922.

[4] If such a limit exists it would be of extremely great interest.

A Determination of the Number of Alpha Particles per Second Emitted by Thorium C of Known Gamma Ray Activity. A. G. SHENSTONE and H. SCHLUNDT. (*Phil. Mag.,* June, 1922.)—"Thorium C and its products produce, in the course of disintegration, alpha rays of ranges 8.6 centimetres and 5.0 centimetres in air, in the proportion of 65 to 35. At the same time they produce hard gamma radiation. Radium C similarly emits hard gamma radiation and alpha particles of range 6.96 centimetres and 3.8 centimetres, the latter, however, appearing in negligible numbers." Since the number of alpha particles emitted per sec. per mg. is known for Radium C, it is possible to compute the corresponding number for Thorium C by making a comparison of the number of scintillations caused in a minute on a zinc sulphide screen by the impact of the alpha particles from the two sources, the relative gamma ray activity being measured at the same time. The active deposit of thorium C was obtained by rotating a nickel disc for thirty minutes in a solution of radiothorium To provide radium C, radium emanation was allowed to decay overnight in a glass tube. The active matter deposited on the walls was dissolved in dilute hydrochloric acid, and a nickel disc stirred the solution for a few minutes.

To avoid making large counts of scintillations a rotating wheel with a slot on its circumference was interposed between the active material and the zinc sulphide screen. The alpha particles could reach the screen only through the slot. The control measurements for gamma ray activity were made with an electroscope. "Thorium C should fall to half value in 60.5 minutes and Radium C in 19.5 minutes. Actually we obtained decay curves giving periods of 60 to 61 minutes for thorium C and 19.5 to 20.2 for Radium C."

The mass of thorium C, which has the same activity as 1 mg. of radium and its products as measured by gamma rays that have in both cases traversed 3.3 mm. of lead, emits in one sec. 30,700,000 alpha particles of 8.6 cm. range.

G. F. S.

Viscosity of Air in a Transverse Electric Field. SATYENDRA RAY. (*Phil. Mag.,* June, 1922.)—Quincke found that both parallel and perpendicular to the electric lines of force the viscosity of liquids become greater in an electric field, "If polarization physically means an orientation of molecules or a kind of tidal distortion of the molecule, a change in the effective area of the cross-section and a consequent change in the viscosity with the electric field might be expected." To seek any change in the viscosity of air a transpiration method was used. The application of a field of 580 volts potential difference to two plates .31 millimetre apart failed to make even the change of a single second in the time of efflux, which was 9 minutes 39 seconds. There seems to be no change in the viscosity of air equal to as much as .3 per cent., owing to the application of the field.

G. F. S.

NOTES FROM THE RESEARCH LABORATORY EASTMAN KODAK COMPANY.*

THE DRYING AND SWELLING OF GELATIN.[1]

Preliminary Note by S. E. Sheppard and F. A. Elliott.

[ABSTRACT.]

THE theory of drying and swelling of gelatin gels is discussed, and observations are reported which make it more reasonable to believe that a so-called "case-hardening effect" is responsible for the maintenance of the original shape on swelling and drying. The initial stages of the drying process take place at edges and corners, thus creating a drier, rigid framework which guarantees the shape, and hence, submicroscopic structures inherent in gelatin are unnecessary to account for this phenomenon.

Talc and Soapstone in 1921. (*U. S. Geological Survey Press Notice.*)—The production of talc and soapstone in 1921 showed a great decline as compared with that in 1920. The quantity sold was the smallest since 1908 and was about 40 per cent. less than the average for the five preceding years.

The total quantity of talc and soapstone sold in 1921 was 126,000 tons, valued at $1,821,000, as compared with 211,000 tons, valued at $3,035,000, in 1920. This represents a decrease of 40 per cent. in both quantity and value. Vermont, which since 1917 has been the largest producer, maintained its position by producing 38 per cent. of the total quantity. New York produced 33 per cent. of the quantity sold, but for the first time took second place in the value of its product. Virginia, which produced 14 per cent. of the total, ranked next to New York in quantity, but for the first time led in the value of its output, owing to the fact that the soapstone industry in that State was not nearly so much affected as the ground talc industry, on which the other principal producing states depend.

The quantity of ground talc sold by producers in 1921 was 106,900 tons, valued at $1,181,000, as compared with 178,500 tons, valued at $2,143,000, in 1920. A canvass of the producers made to determine the quantity of talc consumed in 1921 by different industries shows that the paper industry used 38 per cent. of the total, and that the average value was about $10.60 a ton. Most of the supply was obtained from Vermont and New York. The paint industry, which requires a high grade of talc, used 23 per cent. of the total. Nearly all the supply was obtained from New York, and the average value was about \$14.10 a ton. The roofing industry consumed 18 per cent. of the total and drew its supply almost entirely from Vermont. The requirements for talc used in this industry are not exacting, as is shown by the average value, which was only \$8 a ton. The rubber industry used a large quantity of talc for filler, and in 1921 consumed 9½ per cent. of the total. Vermont furnished most of the supply, which had an average value of about \$9.50 a ton. The textile industry used about 4 per cent. as a filler for cotton cloth. The average value was about \$9.40 a ton. Only 2½ per cent. of the domestic output was used for toilet powder, the demand for talc for that use having been supplied largely by imported material. California supplied most of the demand for domestic talc for this purpose, and the average value was \$18.60 a ton.

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* Communicated by the Director.

[1] Communication No. 131 from the Research Laboratory, Eastman Kodak Company and published in *J. Amer. Chem. Soc.*, Feb., 1922, p. 373.

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On the Elementary Quantity of Electricity. R. BAER. (*Ann. d. Physik,* No. 3, 1922.)—It is now generally recognized that electricity has an atomic structure. Upon this foundation is built the modern theories of atomic structure. Quantities of electricity cannot be changed continuously, but only by the addition or subtraction of one or more elementary quantities, just as the weight of a mass of water cannot be changed continuously but only by the addition or removal of one or more molecules. Moreover the body of physicists are agreed on the magnitude of the elementary quantity of electricity. It is 4.774×10^{-10} electrostatic units, for our own Millikan has measured it to a few tenths of a per cent. There has been, however, one protest registered against the validity of this conclusion. Ehrenhaft, in Austria, and his followers for a dozen years have been claiming to find a quantity of electricity, much smaller than Millikan measured, even perhaps as small as one two-thousandth of it. This is an important matter, and in science decisions are made by evidence and not by " the infallibility of the odd man " or even by a preponderance of votes as is the case when we go to the polls.

The whole question has been examined by the author of this paper, and he comes to the conclusion that the atomic structure of electricity rests on a firm foundation. The contrary results of Ehrenhaft and Miss Parankiewicz have arisen from their failure to make allowances for the Brownian Movements, and from the assumption of too large densities. " There is not the least evidence for the existence of quantities of electricity smaller than the charge of an electron." This is comforting especially for those who were trained at first to look on atoms as fine little billiard balls and have been subsequently constrained to adjust their conceptions to the belief that the atom is a miniature solar system and who were apprehensive lest still later the electron with its charge of electricity should turn out to be of an unexpected complexity.

G. F. S.

NOTES FROM THE U. S. BUREAU OF CHEMISTRY.*

FUNCTIONAL EVIDENCE OF THE PHYLOGENY OF THE NERVOUS SYSTEM AS SHOWN BY THE BEHAVIOR AND RESISTANCE OF THE DEVELOPING RAT TO STRYCHNINE.[1]

By E. W. Schwartze.

[ABSTRACT.]

The reaction to strychnine of the very young rat is not unlike that shown by animals lower than mammals. This prototype reaction may be considered as functional evidence of the phylogeny of the nervous system. Very young rats also have a relatively high natal resistance to the action of strychnine which declines as the animals grow older until they reach a certain age. These observations agree with many scattering data on other animals, including man.

After the decline in natal resistance, the rat develops a post-natal resistance. Those animals for which sufficient data regarding the toxicity of strychnine exist showed this curious coincidence—a post-natal resistance to strychnine was developed in those animals in which the pyramidal tract is in the dorsal funiculus, while such resistance was not developed in animals having the pyramidal tract in the lateral funiculus. The data were not sufficient to permit analysis of cases where the pyramidal tract is in the ventral funiculus.

The observations suggest that strychnine tests would be useful, particularly in conjunction with other methods, in studying functional development of the central nervous system.

SEPARATION AND DETERMINATION OF SATURATED AND UNSATURATED FATTY ACIDS BY MEANS OF THE LEAD SALT-ETHER METHOD.[2]

By Walter F. Baughman and George S. Jamieson.

[ABSTRACT.]

The percentages of saturated and unsaturated acids in a fatty oil and the iodine number of the unsaturated acid fraction are

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* Communicated by the Chief of the Bureau.

[1] Published in *J. Pharmacol.*, 19 (1922), 273.

[2] Published in *Cotton Oil Press*, 6 (1922), 41.

more characteristic for many oils than some of the other values usually determined.

From a study of the lead salt-ether method for making this separation the authors have developed several modifications which it is believed increase the accuracy of the results.

This method is based on the solubility of the lead salts of the liquid unsaturated acids, oleic, lineolic, linolenic, and clupanodonic, in ether, in which the lead salts of the solid saturated acids, myristic, palmitic, stearic, arachidic, lignoceric, etc., are practically insoluble. Satisfactory results cannot be obtained with cocoanut, palm kernel and similar oils which contain lauric, capric, caprylic and caproic acids because the lead salts of these acids are appreciably soluble in ether.

THE EFFECT OF NITRATES APPLIED AT DIFFERENT STAGES OF GROWTH ON THE YIELD, COMPOSITION, AND QUALITY OF WHEAT.[3]

By Jehiel Davidson.

[ABSTRACT.]

THE period between the resumption of growth of wheat in the spring and the time of heading was divided into three sub-periods. Each of three corresponding sets of plots received nitrates at one of these sub-periods. The results thus obtained show that:

1. The effectiveness of nitrates in increasing yields decreases consistently as the time of their application approaches the stage of heading.

2. The effectiveness of nitrates in increasing the protein content ($N \times 5.7$) of the grain increases as their effectiveness in increasing the yield decreases.

ANALYSES OF AUTHENTIC PEANUT OILS.[4]

By George S. Jamieson and Walter F. Baughman.

[ABSTRACT.]

IT is important for those interested in the fatty oil industry to know the limits of the variations in the chemical and physical characteristics of oils. The many results recorded in the literature show wide variations, but in many cases information on the treatment of the samples or on their authenticity is lacking. The composition of some may have been modified by storage. For these reasons the American Oil Chemists' Society requested the Bureau of Chemistry to determine the chemical and physical characteristics of authentic samples of the important commercial oils. Among the oils analyzed were 22 samples of authentic peanut oils collected during 1920, 1921, and 1922. The results show that there is a distinct difference between the values for oil from Virginia type peanuts and those for oil from Spanish type peanuts. The results for each type, however, are uniform. The averages of the results are given in the following table:

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[3] Published in *J. Am. Soc. Agron.*, 14 (1922), 118.

[4] Published in the *Cotton Oil Press*, 6 (1922), 34.

	Titer.	Refractive index at 20° C.	Specific gravity, 25/25°C.	Iodine number (Hanus).	Saponification value.	Saturated acids. Per ct.	Unsaturated acids. Per ct.	Iodine number of unsaturated acids.
All Samples	31.3	1.4691	0.9133	93.2	187.3	18.0	77.3	118.9
Variation:								
High	32.0	1.4720	.9148	98.2	188.4	20.6	79.5	125.6
Low	30.5	1.4670	.9123	89.0	186.6	15.3	74.2	109.0
Virginia type Samples				92.0		16.1	79.1	114.4
Variation:								
High				96.8		16.6	79.5	121.1
Low				89.0		15.3	78.7	109.0
Spanish type Samples				93.7		20.1	75.2	122.7
Variation:								
High				96.2		20.6	76.6	125.6
Low				90.1		18.7	74.2	120.2

A New Apparatus for the Demonstration of Gravitational Attraction. T. WULF. (*Physikal. Zeit.*, April 1, 1922.)—The Cavendish apparatus, consisting of a bar suspended by a thin wire and swinging in a horizontal plane furnishes a method of measuring very small forces. At the end of the bar is a metallic sphere which is attracted by a mass placed near it, with the result that the bar is turned from its original position. In the skilled hands of C. V. Boys and of Burgess, wonderfully accurate determinations have been made, but the instrument requires careful handling. Boys found it necessary to instal his experimental group in a cellar and was compelled to dedicate the hours of the early morning to it in order to avoid the upsetting effect of the traffic of London. The present experimenter is not desirous of making a new determination of the Gravitational

Constant, but he does want an apparatus that will perform well before a class and will not claim too much from the demonstrator.

His general plan is this. A large sphere is brought near to the sphere on the end of the horizontal beam. The force of gravitational attraction makes the beam turn to one side. It swings out to an extreme position and then turns back. At that instant the attracting mass is shifted to the other side of the sphere on the beam and hence accelerates the latter toward its first position. Whenever the beam comes to the end of its swing the attracting mass is shifted, with the result that the amplitudes of the vibration constantly increase. The damping effect of the air, however, comes in play so that eventually it is just counterbalanced by the force exerted by the attracting sphere and the amplitude stays constant. The exact maximum amplitude attainable can be fixed within narrow limits by running it up, on the one hand, and by letting it decrease from too great a value on the other.

Quartz fibres of ultra-microscopic diameters no longer are needed to suspend the horizontal pendulum, but brass wire .1 millimetre in diameter and 15 to 20 centimetres in length suffices. This has the further result that tremors and air currents cease to invalidate the observations. A demonstration apparatus, sitting on a table in front of a class, functions to the extent of producing a deflection of a metre on a scale two or three metres away.

G. F. S.

A New Interferential Method of Measuring the Apparent Diameter of Stars. A. DANJON. (*Comptes Rendus*, May 29, 1922.)—One objection to the Fizeau-Michelson method of determining the angular diameter of stars is that the two interfering beams must be 12 metres apart in order to serve for a star of apparent diameter equal to .01 sec. of arc. The proposal is made to use a Jamin interferometer. The sky is observed through the instrument and the star to be measured is seen upon the field of bright and dark bands. As it moves its brightness changes, becoming a minimum on a dark band and a maximum upon a bright band. The ratio of the two extreme intensities is measured and from this it is possible to calculate the angular diameter of the star. The whole determination, therefore, rests upon photometric measurements.

So far as purely laboratory tests go, the method has stood the trial well, but the prevalent bad weather in France during the past spring has kept the Strasbourg investigator from actual application to a star. Atmospheric agitation may prove an insuperable obstacle to success. The claim is made that for the measurement of Betelgeuse the two interfering beams need be but 10 centimetres distant from each other instead of 3 metres as hitherto. An attempt will be made to measure this star with a telescope having an aperture of only 16 centimetres, when Orion returns to our skies.

G. F. S.

NOTES FROM THE U. S. BUREAU OF MINES.*

PRESSURES OF PETROLEUM PRODUCTS AT ELEVATED TEMPERATURES.

By M. B. Cooke.

As a by-product of an investigation into the nature of "gum-forming" constituents of gasoline, the U. S. Bureau of Mines recorded data showing the pressure that may be developed in a still when gasoline or other oil is subjected to elevated temperatures. Samples of casinghead gasoline, motor gasoline, kerosene, and transformer oil were heated in a small steel bomb, the pressures developed were recorded by a gage, and temperature-pressure curves were made.

These curves show that petroleum products with a low boiling range—such as casinghead gasoline and some of the lighter motor gasolines—generate a higher pressure at a given temperature than water vapor. Petroleum products with a relatively high boiling range, such as kerosene and transformer oil, generate less pressure than water vapor at a given temperature. In general, the pressure generated by petroleum products, when subjected to elevated temperatures, varies inversely with the average boiling point of the product. The temperature curves, as well as the distillation range curves, are not parallel, owing to the carrying composition of the products. The complete report illustrated graphically may be obtained from the Bureau of Mines.

CAUSE AND PREVENTION OF DETERIORATION OF PORTLAND CEMENT.

By W. M. Meyers.

The Bureau of Mines has completed an investigation of the cause of the deterioration of Portland cement during storage and transportation and suggests in a mimeographed report means for preventing such waste. French manufacturers recognize the deleterious effect of climatic conditions on Portland cement and endeavor to send their product direct to the point of consumption.

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* Communicated by the Director.

The Bureau suggests two improvements in the practice of handling cement: (1) Storage and transportation of the cement in bulk; (2) storage and transportation of the cement in the form of unground clinker, grinding to be done at destination. The first method results in a decrease in hydration of cement, as the exposed surface is less. Shipment should be made in a tight closed car, and the cement at all points protected from moisture. The second method has the distinct advantage that the quality of cement produced from stored clinker is higher, on account of hydration of free lime in the clinker, and the grinding cost is lower because the mechanical disintegration of clinker during storage makes grinding easier. The report has a bibliography, and is now available.

PROPERTIES OF OKLAHOMA CRUDES.

By E. W. Dean, A. D. Bauer, M. B. Cooke, and C. R. Bopp.

As part of a comprehensive survey of American crudes, the United States Bureau of Mines recently completed a survey of Oklahoma crude oils. The Eastern, Rocky Mountain, Northern Texas, Northern Louisiana, Arkansas, and Kansas fields had been covered previously, and the data published.

The distillation of the Oklahoma crudes showed a narrow gravity range, mostly between 30 and 40° Baumé, with a minimum of 28.6° and a maximum of 52.1°. The average figure was 35.7°, which is noticeably higher than the average figure of 31.8° for Kansas crudes.

Sulphur content varied from 0.06 to 0.72—about one-half of the samples ranging from 0.1 to 0.2. The viscosity and pour tests showed a moderate degree of variation through the series, but none of the oils is exceptionally viscous.

To the refiner the most important property of crude petroleum is its content of gasoline and naphtha. The Oklahoma series makes a particularly favorable showing in this respect, as the average gasoline content is 27.6 per cent., some oils containing as much as 40 per cent.

Less than half of the Oklahoma crudes sampled require blending with volatile products from natural gas in order to make them a well-balanced motor fuel. The carbon residue varies from 3 to 13 per cent., mostly above 6 per cent., hence most Oklahoma crudes could probably be made to yield a cylinder stock, some without special treatment, others with chemical treatment.

On the basis of relative gravities or viscosities of selected distillation fractions, practically all the Oklahoma crudes sampled are intermediate between the crudes of the paraffin-base type, such as Pennsylvania and West Virginia crudes, and those of the naphtha-base type, such as the California crudes, are exceptionally uniform in gravity.

The complete report on the Oklahoma crudes with tables of distillation results may be obtained in mimeographed form from the Bureau of Mines.

Barium and Strontium.—A report on Canada's resources recently issued by its Mines Branch, Department of Mines, shows that the hitherto exploited occurrences of barium and strontium minerals in Canada are all situated in Eastern Canada, and chiefly in Ontario and Nova Scotia. Barytes mining has had its greatest development in Nova Scotia, the important deposits at Lake Ainslie having furnished the bulk of the barytes produced in Canada. A number of small, scattered deposits occur in southeastern Ontario, but these are not considered of any great economic importance. In recent years, important bodies of barytes have been discovered in northern Ontario. Unfortunately some of the most promising deposits in this region are situated too far from a railroad to permit of their exploitation at the present time. Large deposits are also stated to occur in British Columbia near Spillimacheen, on the Kootenay Central railway, but no development of these occurrences has taken place.

With the exception of a few hundred tons produced in the Lake Ainslie district, Nova Scotia, there has been practically no output of barytes in Canada, for several years past. The cause for this would appear to be not lack of barytes, but the comparatively low price at which barytes has been selling. Barytes is produced very cheaply in Missouri, Georgia and Kentucky, the mineral occurring as lumps in clay and being dug out by hand (Missouri) or by steam shovel (Georgia). Canadian Barytes cost more to mine, and there is in addition, the remoteness of many of the deposits from the consuming centres to be considered. Also, Canadian vein barytes is often harder and more difficult to grind than the soft Missouri barytes.

Barytes finds its greatest use in the manufacture of paints and rubber goods. In these industries it is used either in the form of ground barytes or as lithopone, a product of barytes and zinc blende.

The only strontium mineral of importance occurring in Canada is the sulphate of strontium, celestite, which is only known in possible economic quantities in southeastern Ontario. The known deposits are not very large, but, in one or two instances, are regarded as capable of successful exploitation, should an active demand for celestite arise. Most of the celestite consumed on the American continent is imported from England, and is used principally for the preparation of strontium hydrate which is employed in the refining of beet sugar. In the manufacture of fireworks strontium salts are used to produce red fire.

R.

Weather Forecasting. (*U. S. Department of Agriculture Press Service, Clip Sheet No. 210.*)—Instruction embracing a course in weather forecasting based on publications of the Weather Bureau and intended to increase the efficiency of pilots and improve the navigation of power boats generally, has recently been prepared by the United States Power Squadrons, a national association of power-boat owners, which was organized in 1915. This organization requires that applicants for membership shall pass an oral examination in piloting and chart work and encourages its members to study weather forecasting.

A pamphlet for which the Weather Bureau furnishes the authority, covering certain aspects of meteorology and forecasting, is issued to each member, and talks on weather forecasting are given from time to time to classes in different cities. Instruction to advanced classes in dead-reckoning and astronomical navigation includes questions on the laws of storms and general weather forecasting. The aim of the association is to raise the standard of skill in handling and navigating power boats, to coöperate with the Government in enforcing regulations relating to navigation, and to stimulate interest in activities tending to build up our merchant marine and navy.

R.

Fossil Flower in Rock.—Fossil flowers are such rare discoveries in the United States that the finding of a dogwood "flower" in a fragment of rock from the Glenrock coal field, Converse County, Wyoming, is of interest. Dr. F. H. Knowlton, a paleobotanist of the United States Geological Survey, identified the fossil as a species of *Cornus*, a typical genus of the dogwood family.

There are some forty or fifty living species of the genus *Cornus*, which is widely distributed over three continents of the Northern Hemisphere, and has one representative south of the Equator, a species in Peru. The leaves of more than twenty fossil species of Cornus have been found in North America, but the dogwood flower, just identified, is the first one yet found in the United States. Species of dogwoods first appeared in the middle of the Cretaceous, the geologic period in which dinosaurs lived; in other words the genus *Cornus* seems to have made its first appearance probably more than four million years ago.

R.

THE FRANKLIN INSTITUTE.

MEMBERSHIP NOTES.

CHANGES OF ADDRESS.

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Mr. Frank E. Whitney, Commercial Truck Company, Hunting Park and Rising Sun Avenues, Philadelphia, Pennsylvania.

NECROLOGY.

Mr. A. Stuart Baldwin, Illinois Central R. R. Company, Chicago, Illinois.

LIBRARY NOTES.

PURCHASES.

Annuaire des Journaux 35^{e} Année. 1922.

Archimedes. Über Spiralen. Ostwald's Klassiker No. 201. 1922.

Beilstein, F.—Handbuch der organischen Chemie, vol. iv, Ed. 4. 1922.

Biedermann, Rudolf.—Chemiker Kalendar, 2 vols. 1922.

Desargues, G.—Ergebnisse des Zusammentreffens eines Kegels mit einer Ebene. Ostwald's Klassiker No. 197. 1922.

Einstein, Albert.—Theorie der Brownschen Bewegung. Ostwald's Klassiker No. 199. 1922.

Kepler, J.—Grundlagen der geometrischen Optik. Ostwald's Klassiker No. 198. 1922.

Rydberg, J. R.—Emissionsspektren der chemischen Elemente. Ostwald's Klassiker No. 196. 1922.

GIFTS.

L'Academie Royale des Sciences, Annuaire, 1922. Brussels, Belgium, 1922. (From the Academy.)

Acme Lighting Fixture Company, Catalogue No. 20, Distinctive Lighting Fixtures. New York City, New York, 1922. (From the Company.)

American Institute of Consulting Engineers, Constitution and By-laws and List of Members. New York City, New York, 1922. (From the Institute.)

American Institute of Mining and Metallurgical Engineers, Transactions, vol. lxvi. New York City, New York, 1922. (From the Institute.)

American Well Works, Report on Galesburg Municipal Water Works Improvement. Aurora, Illinois, 1922. (From the Works.)

Amsterdam Koloniaal Instituut, Elfde Jaarverslag, 1921. Amsterdam, Holland, 1921. (From the Institute.)

Antioch College, Announcement 1922–1923. Yellow Springs, Ohio, 1922. (From the College.)

Arrow Electric Company, Catalogue No. 19. Hartford, Connecticut, 1922. (From the Company.)

Atkins, E. C., and Company, Incorporated, Saws in the Filing Room, How to Sell a Saw, Silver Steel Saws and Cross-cut and Hand-saws. Indianapolis, Indiana, 1922. (From the Company.)

Babcock and Wilcox, Limited, Steam Generation. London, England, 1922. (From the Company.)

Baylor University, Catalogue 1921–1922 and Announcements, 1922–1923. Waco, Texas, 1922. (From the University.)

Bombay Observatory, Report of the Director for Year Ending December 31, 1921. Bombay, India, 1922. (From the Director.)

Broderick and Bascom Rope Company, Aerial Tramways. St. Louis, Missouri, 1922. (From the Company.)

Brown, David, and Sons, Limited, Machine-cut Gearing, Worm-drive and Worm-wheel Generator. Lockwood, Huddersfield, England, 1922. (From the Company.)

Brown and Tawse, Limited, B and T Reinforced Concrete. London, England, 1922. (From the Company.)

Cambridge Department of Water, Annual Report for the Year Ending March 31, 1921. Cambridge, Massachusetts, 1921. (From the Secretary.)

Canada Department of Mines, Bulletins 34 and 36, and Victoria Memorial Museum Memoir 126. Ottawa, Canada, 1922. (From the Department of Mines.)

Canning, W., and Company, Limited, Prevention of Rust. Birmingham, England, 1920. (From the Company.)

Central Scientific Company, Catalogue R, Chemicals. Chicago, Illinois, 1922. (From the Company.)

Chalmers and Williams, Catalogue H, Drop Bars, Feeders and Screens. Chicago Heights, Illinois, 1922. (From the Company.)

Cheltenham Works, Limited, Relmac and Super Relm Lathes and Accessories. London, England, no date. (From the Works.)

Chicago, Burlington and Quincy Railroad Company, Sixty-eighth Annual Report. Chicago, Illinois, 1922. (From the Company.)

Clark, William J., Commercial Cuba. New York City, New York, 1898. (From Mr. John J. Bradley.)

Clarkson Memorial College of Technology, Clarkson Bulletin, Catalogue Number for 1922. Potsdam, New York, 1922. (From the College.)

Cohen, Charles J., Rittenhouse Square, Past and Present. Philadelphia, Pennsylvania, 1922. (From the Author.)

Colorado School of Mines, Quarterly, July, 1922. Golden, Colorado, 1922. (From the School.)

Connersville Blower Company, Catalogue No. 20, Connersville Cycloidal Pumps, Connersville, Indiana, no date. (From the Company.)

DeLaval Steam Turbine Company, Sewage Pumps. Trenton, New Jersey, 1921. (From the Company.)

Dexter, I. H., Company, Flexible Couplings. Goshen, New York, 1922. (From the Company.)

Dixon, Joseph, Crucible Company, Graphite for 1921. Jersey City, New Jersey, 1922. (From the Company.)

Dixon, William, Incorporated, Catalogue of Dixon Tools. Newark, New Jersey, 1919. (From the Corporation.)

Dust Recovering and Conveying Company, Bulletins 503 and 507. Cleveland, Ohio, 1922. (From the Company.)

Elliott Company, Bulletins C and N–1. Pittsburgh, Pennsylvania, 1921. (From the Company.)

Erie and Pittsburgh Railroad Company, Sixty-fourth Annual Report. Erie, Pennsylvania, 1922. (From the Company.)

Florida East Coast Railway Company, Annual Report for 1921. St. Augustine, Florida, 1921. (From the Company.)

Ford Meter Box Company, Ford System of Meter Settings and Ford Meter Testing Machine. Wabash, Indiana, no date. (From the Company.)

Ford Regulator Corporation, Bulletin Catalogue of Steam and Water Valve Specialities. New York City, New York, 1922. (From the Corporation.)

Foxboro Company, Incorporated, Bulletin No. 104–1 Thermometers. Foxboro, Massachusetts, 1921. (From the Company.)

John Fritz Medal Board of Award, John Fritz Medal Book. New York City, New York, 1922. (From the Board.)

Garvin Machine Company, The Bright Internal Grinder. New York City, New York, 1922. (From the Company.)

General Electric Company, Bulletin No. 43856, High-powered Searchlights Beck System, Commercial Uses for Searchlights and 36-inch and 34-inch Intensity Searchlight Shaft Control. Schenectady, New York, no date. (From the Company.)

General Railway Signal Company, G-R-S Automatic Train Control. Rochester, New York, 1922. (From the Company.)

Georgia School of Technology, Catalogue 1921–1922 and Announcements 1922–1923. Atlanta, Georgia, 1922. (From the School.)

Gledhill-Brook Time Recorders, Limited, Catalogue of Time Recorders. Huddersfield, England, no date. (From the Company.)

Grindle Fuel Equipment Company, Grindle Powdered Fuel Equipment. Harvey, Illinois, 1922. (From the Company.)

Halstead, Murat, The Story of Cuba. Chicago, Illinois, 1896. (From Mr. John J. Bradley.)

Haverhill City Engineer, Annual Report for the Year Ending December 31, 1921. Haverhill, Massachusetts, 1922. (From the Engineer.)

Hupp Motor Car Corporation, The Use of Metals. Detroit, Michigan, 1922. (From the Corporation.)

India Geological Survey, Records, vol. liii, Part 2. Calcutta, India, 1922. (From the Survey.)

India Meteorological Department, Monthly Rainfall of India for 1920. Calcutta, India, 1921. (From the Department.)

Indian Railway Conference Association, Proceedings and Agenda of Lucknow Meeting, February, 1922. Bombay, India, 1922. (From the Secretary.)

International Time Recording Company, Limited, Guarding the Minute. London, England, 1922. (From the Company.)

Ivanhoe-Regent Works of General Electric Company, Catalogue No. 366, Crystal Roughed and Clear Line Electric and Gas Shades. Cleveland, Ohio, 1922. (From the Works.)

Japanese Department of Railways, Annual Report for the Year Ending March 31, 1919. Tokyo, Japan, 1920. (From the Department.)

Kilbourne and Jacobs Manufacturing Company, Bulletins 3101 and 3102 on Industrial and Quarry Cars. Columbus, Ohio, 1919. (From the Company.)

Kingsbury Machine Works, Catalogue C, Kingsbury Thrust Bearings. Philadelphia, Pennsylvania, 1922. (From the Works.)

Leeds and Northrup Company, Potentiometer Pyrometers, Catalogue 87. Philadelphia, Pennsylvania, 1922. (From the Company.)

Littell, F. J., Machine Company, Automatic Feeds, Special Machinery. Chicago, Illinois, 1922. (From the Company.)

Liverpool Engineering Society, Transactions, vol. xlii. Liverpool, England, 1921. (From the Society.)

Liverpool Literary and Philosophical Society, Proceedings of Sessions 1918–19, 1919–20, 1920–21. Liverpool, England, 1921. (From the Society.)

London Institute, Report of the Council, 1922. London, England, 1922. (From the Institute.)

London Steam Turbine Company, Bulletin 14. Troy, New York, 1922. (From the Company.)

Mashek Engineering Company, Catalogue No. 5, Briqueting Machinery and Plants. New York City, New York, 1922. (From the Company.)

Michigan Central Railroad Company, Seventy-sixth Annual Report of Board of Directors. Detroit, Michigan, 1922. (From the Company.)

Musick, John R., Hawaii Our New Possessions. New York City, New York, 1898. (From Mr. John J. Bradley.)

National Canners Association, Vitamins in Canned Foods. Washington, District of Columbia, 1922. (From the Association.)

National Malleable Castings Company, Booklet 69, Coiled Spring Journal Box. Cleveland, Ohio, 1922. (From the Company.)

National Water Main Cleaning Company, Cleaning of Water Mains. New York City, New York, 1922. (From the Company.)

Naugle Pole and Tie Company, Butt-Treatment of Cedar Poles. Chicago, Illinois, no date. (From the Company.)

New Bedford Water Board, Report for the Year Ending December 31, 1921. New Bedford, Massachusetts, 1922. (From the Board.)

New South Wales Royal Society, Journal and Proceedings, vol. liv, 1920. Sydney, Australia, 1920. (From the Society.)

New York Bureau of Statistics and Accounts, First and Thirteenth Annual Reports for Second District and Report of First District. New York City, New York, 1922. (From the Bureau.)

New York Central Railroad Company, Report of Board of Directors for 1921. New York City, New York, 1922. (From the Company.)

New Zealand Census and Statistics Office, Official Year-book 1921–22. Wellington, New Zealand, 1922. (From the Office.)

Nobbs, George, Limited, Electrical Heating Pamphlet. London, England, 1922. (From the Company.)

Ohio Geological Survey, Bulletins 23 and 24, Fourth Series. Columbus, Ohio, 1921. (From the State Geologist.)

Oliver Machinery Company, Bulletin 6 of Saws. Grand Rapids, Michigan, 1922. (From the Company.)

Ontario Bureau of Mines, General Index to Reports, vol. i to xxv, 1891–1916. Ontario, Canada, 1921. (From the Bureau.)

Pelton Water Wheel Company, Bulletin 17 of Pelton Water Wheels and Reaction Turbines. San Francisco, California, 1922. (From the Company.)

Penberthy Injector Company, Catalogue 29. Detroit, Michigan, 1922. (From the Company.)

Pennsylvania Bureau of Statistics and Information, Report on Productive Industries, Railways, Taxes and Assessments, Waterways and Miscellaneous Statistics for 1920, Report of Paint and Oil, 1919–1920, and Pennsylvania Forestry, 1918–1919. Harrisburg, Pennsylvania. (From the Bureau.)

Pennsylvania Railroad Company, Seventy-fifth Annual Report for 1921. Philadelphia, Pennsylvania, 1921. (From the Company.)

Philadelphia National Bank, Philadelphia, The Sesqui-Centennial City. Philadelphia, Pennsylvania, 1922. (From the Bank.)

Philadelphia Rapid Transit Company, Report on the Valuation of Property. Philadelphia, Pennsylvania, 1922. (From the Company.)

Pittsburgh Tool Steel Wire Company, Cold Drawn Tool and Alloy Steels Polished Needle Bar Stock Drill Rods. Monaca, Pennsylvania, 1922. (From the Company.)

Rockefeller Foundation, A Review for 1921. New York City, New York, 1922. (From the Foundation.)

Roto Company, Roto Tube Cleaners. Hartford, Connecticut, 1922. (From the Company.)

Rowson, Drew and Clydesdale, Limited, Elevating and Conveying Machinery. London, England, 1922. (From the Company.)

Royal Society of Canada, Proceedings and Transactions of Meeting of May, 1921. Toronto, Canada, 1921. (From the Society.)

Schutte and Koerting Company, Bulletin No. 4L. Philadelphia, Pennsylvania, 1922. (From the Company.)

Shannon, J. Jacob, and Company, Derricks, Engines, and Equipment. Philadelphia, Pennsylvania, 1922. (From the Company.)

St. Paul Board of Water Commissioners, Fortieth Annual Report for Year Ended December 31, 1921. St. Paul, Minnesota, 1922. (From the Commissioners.)

Sandycroft Limited, Automatic Drop-bar Grizzly-feeders and Screens. Sandycroft, England, no date. (From the Company.)

Skinner, M. B., Company, Catalogue of Pipe Repairs, Reseating Tools and Specialities. Chicago, Illinois, 1922. (From the Company.)

Smith, T. L., Company, Smith Tilting Mixer, Smith Non-tilting Mixer and Pavers. Milwaukee, Wisconsin, no date. (From the Company.)

Smithsonian Institution, Explorations and Field-work of the Smithsonian Institution in 1921. Washington, District of Columbia, 1922. (From the Institution.)

Somerville Street Commissioner, Annual Report for 1921. Somerville, Massachusetts, 1922. (From the Commissioner.)

South Australia Department of Mines, Mining Review for Half-year Ended December 31, 1921, and Bulletin No. 9, The Iron Ore Resources of South Australia. Adelaide, Australia, 1922. (From the Department.)

Staffordshire Iron and Steel Institute, Proceedings of 1920–21 Sessions, vol. xxxvi. Walsall, England, 1921. (From the Institute.)

Standard Oil Company, Stanolind Paving Asphalt. Chicago, Illinois, 1922. (From the Company.)

State College of Washington, Annual Catalogue, 1922. Pullman, Washington, 1922. (From the College.)

Stothert and Pitt, Limited, Road Making Machinery, Catalogue M.D. 106. London, England, 1922. (From the Company.)

Strong, Kennard and Nutt Company, Safety Equipment Catalogue "D." Cleveland, Ohio, 1922. (From the Company.)

Sweets Catalogue Service, Incorporated, Sweet's Engineering Catalogue, Eighth Annual Edition. New York City, New York, 1922. (From the Publishers.)

Syracuse University, Catalogue 1921–22. Syracuse, New York, 1922. (From the University.)

Tabor Manufacturing Company, Power Squeezing Molding Machine. Philadelphia, Pennsylvania, no date. (From the Company.)

Taylor Instrument Companies, General Industrial Catalogue of Tycos Instruments. Rochester, New York, 1922. (From the Companies.)

Temple University, Annual Catalogue, 1922. Philadelphia, Pennsylvania, 1922. (From the University.)

Templeton, Kenly and Company, Limited, Simplex Jacks. Chicago, Illinois, no date. (From the Company.)

United States Air Service. Pamphlets 334, Report on Wind-tunnel Test of U. S. A. 27-C Modified Airfoil and 339, Temperature Effect on Capillaries of Liquid and Vapor Pressure Thermometers. Washington, District of Columbia, 1922. (From the Chief of Air Service.)

University of Arizona, Annual Catalogue 1921–1922. Tucson, Arizona, 1921. (From the University.)

University of Cincinnati, University Record, April, 1922, Parts 1, 2, 4, 5, 6, 7. Cincinnati, Ohio, 1922. (From the University.)

University of Idaho, Annual Catalogue 1921–22. Moscow, Idaho, 1922. (From the University.)

University of Missouri School of Mines and Metallurgy, Bulletin for January, 1922, A Symposium on Mining and Metallurgical Education. Rolla, Missouri, 1922. (From the University.)

University of Nevada, Catalogue 1922–1923. Reno, Nevada, 1922. (From the University.)

University of Sydney. Reprints of Papers from the Science Laboratories, 1916–1917 to 1919–1920, vols. i and ii. Sydney, Australia, 1921. (From the University.)

University of Wyoming, Catalogue for 1922. Laramie, Wyoming, 1922. (From the University.)

Wanamaker Institute, Catalogue 1922–1923. Philadelphia, Pennsylvania, 1922. (From the Institute.)

Webster, Warren, and Company, Steam Heating a Manual of Practical Data. Camden, New Jersey, 1922. (From the Company.)

Whitcomb, George D., Company, Locomotives. Rochelle, Illinois, no date. (From the Company.)

Wright Motors, Limited, Electrical Specialties. Halifax, Nova Scotia, 1922. (From the Company.)

BOOK NOTICES.

L'Azote: La Fixation de l'azote atmosphérique et son avenir industriel. By Louis Hackspill, University of Strasbourg. 261 pages, indexes, appendixes, 39 illustrations and many tables, 12mo. Paris, Gauthier, Villars et Cie. Price 14 francs, net.

The war awakened many of the greater nations to the importance of the nitrogen fixation problem. Scientists had been calling like prophets in the wilderness, but except in Germany, their voices had fallen on dull ears. This book is one of the encouraging instances of the appreciation of the danger of the exhaustion of one of the main sources of the world's supply of nitrogen compounds, the Chile nitrates. It is a very interesting and commendable treatise. Written for a wider public than the professional chemist, it does not enter into the physical chemistry as deeply as Creighton does in his paper in this Journal, but it is evident that the author has searched the literature thoroughly and with full understanding, and he has the capacity to present his knowledge in a form intelligible to the general reader. The book is part of the second series of the Léauté Encyclopedia, and will be followed by others on applied science. The several works are not intended for the exclusive use of the trained expert, nor to furnish a complete statement of the subject treated, but to deal as occasion arises with the important features thereof. The dominant note is "selection."

English-speaking chemists are still wondering why their French brethren call nitrogen "azote." The term is not only highly inappropriate, but the general adoption of the other term would seem to leave no excuse for continuance. Our author, indeed, recognizes the incongruity of the title, for he says: "At present we can say that no godfather was worse inspired than Lavoisier when he gave the name azote to a substance so active in its chemical relations, and as necessary to the function of life. From this point of view, we may be reconciled to the fact that chemists nowadays do not know Greek." In terming nitrogen active the author, of course, refers to its many compounds, and not to the element in the free state. Even in this condition, however, it is not so distinctly poisonous as to justify the name which Lavoisier gave it. Fortunately, French chemists have given up writing "Az" as the symbol of the element, but they still retain the use of superiors, while all the rest of chemists use inferiors for designating numbers of atoms.

Turning to the text, it is found to contain an extensive and clear presentation of the many forms of nitrogen fixation that have been proposed. Beginning with a discussion of the food problem, especially as related to nitrogen supply, the warnings of Sir William Crookes are noted, and tables given to show how far his prophecies have been realized. The nitrogen cycle and the function of the modules in the roots of legumes are described, after which the properties of nitrogen and of certain nitrides are given. Separate chapters are devoted to the several processes that have been suggested for the purposes of fixation. The up-to-date character of the work is shown by the inclusion of a full account of the Bucher method of producing cyanides. A great deal of interesting matter is included in the description of the Haber process, which has filled such a striking and important rôle in the last few years. The history is given in outline, and considerable information as to the details of the methods, but, as might be expected, many points are left without discussion, inasmuch as the German authorities have succeeded in keeping their important secrets very closely. It is noted, for example, in one of the appendixes, that Haber himself advised the German authorities against installing a plant in one of the possessions in the far East, although power sufficient for producing 100,000 tons of ammonium sulphate was available, his reason being that it would not be possible to obtain the technical skill for operating the works.

A short account is given of the explosion at Oppau. Mention is made of the statement by the Germans of the cause being the removal of a mass of ammonium nitrosulphate, but it is probable that if the experts know the cause they do not intend to tell. An account is given of the Claude process, which originating in France, is being now applied there. A feature of this is the use of very high pressure.

The book is neatly printed on good paper, has a fairly good index and numerous illustrations. A perusal of it will place the reader in possession of the present state of procedure on this very important phase of applied chemistry.

HENRY LEFFMANN.

PRACTICAL ELECTRICAL ENGINEERING; DIRECT CURRENTS. By Harry G. Cisin, M.E. 324 pages, 8vo. New York, D. Van Nostrand Company, 1922. Price, $2.00.

This is one of the non-mathematical books which deal in the simplest manner with electricity and magnetism, and are intended for the use of those who have not progressed beyond arithmetic. Such an effort as this is always hazardous and should be attempted by one who has had sufficient experience in teaching these subjects authoritatively to enable him properly to select and condense his material. This particular book, in addition to the disadvantage of the class to which it belongs, is further prejudiced by the verbose and often uncertain statement of its discussions.

W. M. S.

THE PRINCIPLES UNDERLYING RADIO COMMUNICATION. Prepared by the Bureau of Standards for use of Signal Corps, U. S. Army. Second edition; revised to May 24, 1921. 619 pages, 12mo. Washington, Government Printing Office, 1922.

During the summer of 1918 the first edition of this book, containing then 355 pages, was prepared by Dr. J. H. Dellinger, physicist, Bureau of Standards, and a number of collegiate educators, then associated with the Bureau. It was intended for the training of the enlisted personnel of the Signal Corps for radio work; and has also been found useful as a text-book in schools and colleges.

The first third of this revised edition is occupied with the explanation of the elements of electricity, magnetism, and dynamo-electric machinery. The use of any, but the simplest, mathematics is studiously avoided, not only in this portion of the book, but throughout the subsequent chapters. However, the discussion makes frequent use of graphical methods which are generally excellent.

In the work proper the radio circuit is admirably studied, together with electrical oscillations and their decay, or damping. Both in radio and audio transmission, and reception as well, the character of the decrement is of the greatest importance. While this matter receives full treatment, unfortunately the authors fail to mention that in addition to the logarithmical decrement it has recently been found that a linear, or proportional, decrement also exists, which, as it is made ascendant, increases the purity of wave-form, and freedom from harmonics injurious to transmission.

A book of this character should give especial attention to the nature and propagation of electromagnetic waves; but their discussion here is evasive and brief, almost to the point of confusion; but their excitation and control in the practice of radio communication is clearly and sufficiently discussed, though the description and principles of antenna construction might profitably have been enlarged to cover practice fully.

Decidedly the best section of the book is that devoted to the elements and radio practice of the electron tube. In this new art details of such apparatus are changing so rapidly that present forms need not be given more than passing notice; but it is essential to state thoroughly the principles of the operation of tubes. To this purpose the author of this section has admirably condensed a voluminous literature and given lucidity to many of its obscurities by well-developed graphical illustrations of the operation of these tubes.

So important at this time is the subject of radio communication, it is to be regretted that, at best, this book is an educational futility. Though its joint authorship is wholly competent, and its method is generally lucid—often unusually so—it must confuse the non-mathematical student; and annoy, through its evasions, those prepared to read it properly. The educational exigencies of the War might have excused its first composition; but in this revision the preparatory matter on electricity and magnetism should have been omitted, and the necessary mathematics have been employed which are required for a satisfactory discussion of the physics involved; while the practice could have been relegated to a handbook. The result would have been an authoritative text for military and general use on a subject whose increasing importance will soon rank it among the greatest applications of science. WILBUR M. STINE.

TESTING OF ELECTRICAL MACHINERY FOR NON-ELECTRICAL STUDENTS. By J. H. Morecroft and F. W. Hehre. Fourth edition, 220 pages, 8vo. New York, D. Van Nostrand Company, 1921. Price, $3.00.

This short course in the testing of electrical machinery is given by its authors at Columbia University to students of engineering other than electrical with the purpose of preparing them to deal with electrical details which may be intruded into their specific practice.

The subjects discussed in this course are: Direct and alternating current dynamos; motors, and their auxiliary operating appliances; electricity metres of the several prevalent types; storage batteries, and a suggestion of photometry. The method of the book is to preface or accompany the directions for laboratory testing with a considerable presentation of the electrical physics applied in the particular machine or apparatus.

This edition of the book has benefited by the scrutiny of its use for some ten years in its authors' laboratory, and as a result its discussions are generally conducted with force and clearness. But the informative portions are, under necessity of brevity, so inadequate they must confuse the casually prepared student, and are not necessary for the capable one.

It is to be regretted that this class of book persists in electrical literature, as it will be a means to continue the superficial education of engineers, which has been too prevalent in our institutions. W. M. S.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS. Report No. 127. Aircraft Speed Instruments, by Franklin L. Hunt and H. O. Stearns. 38 pages, illustrations, quarto. Washington, Government Printing Office, 1922.

This report consists of three parts relating respectively to air-speed indicators, the testing of air-speed indicators and the principles of ground-speed measurement.

Part I discusses the different types of instruments which have been proposed for the measurement of air-speed and then gives detailed descriptions of most of the instruments, not only of American but also of British, French, Italian and German manufacture, which have reached the state of extensive use as service instruments. A statistical summary of the tests on air-speed instruments of the pressure type made at the Bureau of Standards during the recent war is given and also a short discussion of the altitude effect on air-speed indicators with a practical table of corrections.

Part II describes the methods of testing air-speed indicators used at the Bureau of Standards, together with the tolerances which service instruments should meet. Experimental data and sample reports showing the results of tests are also given.

Part III discusses the physical principles of ground speed measurement and the methods which have been devised for their practical application to the determination of the ground speed of aircraft.

Report No. 147. Standard Atmosphere, by Willis Ray Gregg. 11 pages, illustrations, quarto. Washington, Government Printing Office, 1922.

The need of a standard set of values of pressure, temperature and density at various altitudes is discussed and the desirability of adopting such values as are most in accord with actual average conditions is pointed out in order that corrections in individual cases may be as small as possible. To meet this need, so far as the United States is concerned, all free-air observations obtained by means of kites and balloons at several stations in this country near latitude 40° N. have been used, and average values of pressure, temperature and density, based upon those observations, have been determined for summer, winter and the year and for all altitudes up to 20,000 metres (65,000 feet).. These values are presented in tables and graphs in both metric and English units; and in the tables of densities there are also included values of density for other parts of the world—more particularly for Europe. A comparison with these values shows that, except in the lowest levels, the agreement is very satisfactory. A further comparison with values of density determined from Toussaint's law of temperature decrease, $t = 15 - .0065z$, in which t is the temperature in °C., and z the altitude in metres, indicates very good agreement with those values up to 10 kilometres. It is therefore recommended that the United States adopt Toussaint's values of density up to 10 kilometres and the values presented in the tables for all higher altitudes.

Report No. 149. Pressure Distribution over the Rudder and Fin of an Airplane in Flight, by F. H. Norton and W. G. Brown. 9 pages, illustrations, plates, quarto. Washington, Government Printing Office, 1922.

This investigation was carried out by the Committee at the Langley Memorial Aeronautical Laboratory for the purpose of determining the loads which occur on the vertical tail surfaces in flight. The method consisted in measuring the pressures simultaneously at twenty-eight points on the rudder and fin by means of a recording multiple manometer. The results show that the maximum load encountered in stunting was seven pounds per square foot on the rudder and fin, and it is probable that this might rise to ten pounds per square foot in a violent barrel roll: but in steady flight the average loads do not exceed 0.6 pounds per square foot. The maximum load on the rudder and fin may occur at the same instant as the maximum load on the horizontal tail surfaces and the maximum normal acceleration. The torsional moment about the axis of the fuselage due to the rudder and fin may rise as high as 250 foot-pounds. The results obtained from this investigation have a direct application to the design of the rudder, fin, and fuselage.

PUBLICATIONS RECEIVED.

Leçons d'Analyse Fonctionelle professées au Collège de France, par Paul Lévy, Professeur a l'École Polytechnique, avec une préface de M. J. Hadamard, membre de L'Institut. 442 pages, 8vo. Paris, Gauthier-Villars et Cie., 1922. Price, 35 Francs.

Hydraulics with Working Tables, by E. S. Bellasis. Third edition, 348 pages, illustrations, 8vo. New York, E. P. Dutton and Company, 1922. Price, $8.00.

Mechanical Testing, by R. G. Batson, Associate of King's College, London, and J. H. Hyde, National Physical Laboratory. Volume 1: Testing of Materials of Construction. The Directly Useful Technical Series. 413 pages, illustrations, plates, 8vo. New York, E. P. Dutton and Company, 1922. Price, $9.00.

L'Azote. La fixation de l'azote atmospherique et son avenir industriel, par Louis Hackspill, Professeur a la Faculté des Sciences de l'université de Strasbourg. Encyclopedie Léauté. 271 pages, illustrations, 12mo. Paris, Gauthier-Villars et Cie., 1922. Price, 14 Francs.

Les Progrès de la Métallurgie du Cuivre, par Auguste Conduché, Professeur a la Faculté des Sciences de Rennes. Encyclopédie Léauté. 254 pages, illustrations, 12mo. Paris, Gauthier-Villars et Cie., no date. Price, 14 Francs.

Petroleum, Where and How to Find It, by Anthony Blum. 367 pages, illustrations, portrait, 12mo. Chicago, Modern Mining Books Publishing Company, 1922. Price, $2.00.

Les Axiomes de la Mécanique Examen Critique. Note sur la propagation de la lumière par Paul Painlevé, Professeur a l'École Polytechnique. 111 pages, 12mo. Paris, Gauthier-Villars et Cie., 1922.

Véritable Interprétation des Théories Relativistes, par Maurice Gandillot. 17 pages, illustrations, 12mo. Paris, Gauthier-Villars et Cie., 1922.

Le Principe de la Relativité et la Théorie d'Einstein, par M. Leon Bloch. 42 pages, 8vo. Paris, Gauthier-Villars et Cie., 1922.

National Advisory Committee for Aeronautics: Technical Notes, No. 101. Comparing maximum pressures in internal combustion engines, by Stanwood W. Sparrow and Stephen M. Lee. 3 pages, illustrations, quarto. No. 103. Simple formula for estimating airplane ceilings, by Walter S. Diehl. 4 pages, diagram, quarto. No. 104. Notes on aerodynamic forces—I. Rectilinear motion, by Max M. Munk. 13 pages, quarto. No. 105. Notes on aerodynamic forces—II. Curvilinear motion, by Max M. Munk. 10 pages, quarto. Washington, Committee, 1922.

Painting Cement Floors. ROY C. SHEELER. (*Textile World,* July, 1922, p. 69.)—It has become quite the custom to harden the cement floors in factories by working finely divided iron filings into the surface layer of the cement. Chemical treatment has also been resorted to. Both methods help to prevent dusting and powdering. But neither of these methods gives as good results as the application of the proper cement filler, and the right cement paint. This may seem strange, but it is nevertheless a fact.

If the pigment of the paint is carefully selected for its resistance to abrasion, if it contains a hardy, tough, rapid-drying water-resisting varnish which fills the pores with a hard glossy film, it will resist the rough wear of trucks and foot traffic as well as or better than, iron filings. Then, too, if there is a choice of colors, the floors can be greatly improved in appearance The other methods cannot be repeated, whereas the painting can be done as often as desired and is comparatively inexpensive.

The State system of distributing weather forecasts, warnings, and other information sent out by the Weather Bureau of the United States Department of Agriculture is being continually extended. There are 91 State broadcasting stations which send our weather reports now in operation, of which 20 are operated by leading newspapers. Negotiations are in progress with 33 additional stations, and most of these, which include 11 newspapers, are expected to be in operation in a short time.

R.

Bitter Milk.—LEROY S. PALMER, of the University of Minnesota (*Jour. Dairy Science,* 1922, v, 201–211), finds that the bitter milk of advanced lactation owes its bitterness to the action of a native enzyme lipase. This enzyme cleaves the fat of the milk quite rapidly even at fairly low temperatures, and liberates the lower volatile fatty acids such as butyric acid. These acids then impart a bitter flavor and a rancid odor to the milk. If the fresh milk be heated for a few minutes at a temperature of 75° C., the enzyme is inactivated, and the bitterness does not develop.

J. S. H.

CURRENT TOPICS.

Grade Crossing to be Eliminated on Federal-Aid Highways. (*Eng. World*, June, 1922, p. 368.)—The grade crossings must go, and they will be eliminated wherever possible on the roads of the Federal-Aid Highway System, which will be built as a result of the passage of the Federal Highway Act. When the roads which form the primary or interstate system are constructed, no grade crossing will be allowed to remain that it is at all practicable to avoid. Every effort will be made to make the roads of the secondary system equally safe, but in this case it is recognized that elimination may not be practicable in all cases.

In making this announcement the Bureau of Public Roads, under whose supervision the fund is allotted and construction is undertaken, is putting into effect a policy which it has long advocated in principle, and whose adoption it has urged with increasing effectiveness upon state highway officials for sometime past. The policy is meeting with hearty coöperation on the part of the states, and the American Association of State Highway Officials by resolution has pledged its best efforts to coöperate to eliminate grade crossings on new construction.

In addition, the policy finds favor among the railroads, some of the leading carriers already having lent cheerful aid in avoiding the construction of more grade crossings.

Instead of grade crossings there will be constructed, wherever possible, in the future either a bridge or an underpass where roadway and railway intersect. Important roads, which now cross and recross railroad lines at grades, hereafter will be located entirely on one side of the railroad even though to do so may increase the cost of construction. State officials, realizing the need of eliminating grade crossings, have stated their desire to coöperate with the department in carrying out this plan.

Where crossings are unavoidable, or where local interests justify construction of highways to cross railroad lines, the road will be so located as to pass over the track or under it. In most instances of this sort the railroads bear one-half of the cost of building the bridge or underpass. R.

Diesel Electric Ferryboat for Service in San Francisco Harbor. (*Marine Engineering*, June, 1922, p. 377.)—The *Golden Gate*, which will be the first large automobile ferryboat in this country to be equipped with Diesel engine electric drive, is expected to begin operations in San Francisco Bay early in the coming summer. She will form part of a fleet of ferryboats operated by the Golden Gate Ferry Company, which will offer a fast service between Sausalito and San Francisco, to form a link between the northern and southern highway systems of the State of California.

The *Golden Gate* will have an overall length of 220 feet and a displacement length of about 207 feet. Her propelling equipment will consist of two 500-brake horsepower Werkspoor Pacific Diesel engines each directly connected to a General Electric Company 360-kilowatt, 250-volt, shunt-wound direct-current generator. The power from these generators will be delivered to two 750-horsepower, 500-volt, 145 to 180 revolutions per minute shunt-wound motors one on each propeller shaft. There will be a 35-kilowatt, 115-volt exciter direct connected to each engine generator and used to furnish power for lights, excitation and engine room and deck auxiliaries.

The boat will represent a radical departure in ferryboat construction, being the first double-ended one where each propeller will be driven separately. The most economical method of propelling such a boat is to have the majority of the power concentrated on the propeller that is actually driving it. Electric drive is the only way in which this can be satisfactorily accomplished and still use the same prime mover for both directions of travel, eliminating duplicate units for ahead and astern travel.

The flexibility of control which is a feature of Diesel engine electric drive has also been fully taken advantage of in this boat. She will be equipped with Ward Leonard control, with stations in both pilot houses as well as in the engine room. R.

Airplane to Locate Alaska's Lost Lakes.—Locating and photographing undiscovered lakes in the national forests of Alaska are the latest uses to which the airplane has been put, says the Forest Service, United States Department of Agriculture.

It has long been known that there are many lakes on the headlands and islands traversed by the inside passage between Seattle and Skagway that do not appear on any map. During the New York-Nome flight, made by Army aviators, lakes were frequently sighted which could not be found on the latest and most authentic maps of the territory. Tales of unknown water bodies are constantly being brought in by trappers and prospectors. Less than a year ago a lake four and a half miles long and one-half mile wide was discovered at the head of Short Bay. This lake has over 1000 acres of surface area and is less than one and a quarter miles from tidewater, yet because of the surrounding country's rough topography has remained unknown and unnamed.

Recognizing that many other of these " lost lakes " may be sources of valuable water power, the Forest Service has laid plans to map this no-man's land of the north by means of aerial photographs. A few days' flight, it is said, will be sufficient to cover the area with a degree of accuracy that would require many years and great expense to accomplish by ordinary methods.

The work, which has been approved by the Federal Power Commission, will be done by seaplane, flying from Ketchikan as a base.

R.

A Study in an American Desert.—One of the driest parts of the United States is what is called the Papago country, a region including about 13,000 square miles in southwestern Arizona, so called because it was long ago inhabited by the nomadic Papago Indians. This broad expanse of desert country, which lies between Gila River and the Mexican boundary, contains many groups of volcanic and other mountains separated by broad alluvial basins, which, though the rainfall is small and the temperature is high, sustain a scant growth of desert plants, including orchard-like groups of strange trees. Here the bold slopes of the mountains, the general absence of watering places, and the peculiar forms of the vegetation impress the traveler strongly with the majesty and the mystery of the desert, and excite his wonder as to the origin and history of the natural features.

A report on this region by Kirk Bryan has just been published by the United States Geological Survey, Department of the Interior, as Bulletin 730-B, under the title " Erosion and Sedimentation in the Papago Country, Arizona." The report describes the geology briefly as a setting for a consideration of the agencies that have produced the forms of the land and presents detailed conclusions as to the mode of origin of the desert landscape. The paper is illustrated with diagrams, views, and maps and should be of interest to all students of topography and physiotherapy, particularly those who are endeavoring to solve problems of erosion by wind and water in desert regions. R.

Sugar in Czechoslovakia (*Sugar,* June, 1922, p. 334.)—The total quantity of sugar exported from Czechoslovakia during the 1920–21 season amounted to 456,767 short tons compared with 375,351 short tons during the 1919–20 season. France provided the most important market, having taken 105,300 tons during the 1920–21 season compared with 166,229 tons during the 1919–20 season.

None of this sugar reached the United States during the 1920–21 season, although 3696 tons were marketed here during 1919–20.

Statistics of the total sugar production in Czechoslovakia for the 1921–22 season are not yet available, but it is reported that 3,830,492 short tons of sugar beets have been used, from which approximately 705,472 tons of raw sugar were produced. During the 1920–21 season the production of sugar in that country amounted to 790,614 tons. R.

Forty Thousand-Gallon Steel Tank Moved on Flat Cars. (*Public Works,* July 8, 1922, p. 29.)—A steel locomotive water supply tank of 40,000 gallons capacity, with a conical bottom terminating in a large diameter riser pipe and supported on four steel columns about 20 feet high, was recently jacked up 20 inches and transferred to temporary support on timber falsework, installed on the adjacent ends of the two standard gauge flat cars, heavily ballasted on the opposite ends, that were brought up on spur trucks close to the water tower on opposite sides. The cars were coupled together by chains and the top-heavy empty tank was ballasted by several yards of gravel deposited on a temporary floor at the bottom of the riser pipe which cleared the rail.

The falsework tower was blocked and wedged to bearing on the inclined bottom of the tank, and the tops of the steel columns were guyed with tackles to the flat cars.

The tank was hauled two miles over the Canadian National Railway to Redpath Junction, British Columbia, without injury, care being taken to adjust the position of the cars when passing around curves by means of turnbuckles connecting the chains. R.

Dust Carried by Wind. (U. S. Department of Agriculture Press Service, Clip Sheet No. 211.)—Dust is carried by the wind for long distances, but not usually in quantities sufficiently large for identification. A sample of the dust that settled thickly on the decks of the Dutch steamship *Yildum* when 250 miles out at sea, in latitude 14–15° N., longitude 22° 10′ W.–21° 31′ W., was recently sent to the Weather Bureau of the United States Department of Agriculture by the captain of the vessel. The dust was undoubtedly blown from the Desert of Sahara, which is in approximately the same latitude as that reported by the *Yildum*. The Weather Bureau receives regular marine weather reports, such as that sent in by this vessel, from ships of 20 nationalities, which coöperate with the bureau in collecting and disseminating information about weather conditions at sea. Two days later the British steamship *Dundrennan* and the Dutch steamship *Hagno,* more than 1500 miles west of the *Yildum*, observed the same phenomenon, although the amount of dust was much smaller. R.

Peanut Oil. (*U. S. Department of Agriculture Press Service, Clip Sheet No. 210.*)—The manufacture of peanut oil has been stimulated a great deal in recent years because of the ravages of the cotton boll weevil in reducing cotton growing in certain sections. Peanuts are grown in place of cotton. Before 1914 very little of the oil was made, only 450,000 pounds being produced in 1912, but by 1918 the quantity turned out by crushers in this country was about 50,000,000 pounds. At the same time imports increased from 7,600,000 to 27,400,000 pounds. R.

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AN ELECTRON THEORY OF SOLIDS.*

BY

J. J. THOMSON, O.M., F.R.S.

Franklin Medalist, Honorary Member of the Institute.

My object in this paper is not so much to elaborate the details of a theory of solids as to point out that the electronic theory of the constitution of the atom leads quite simply and directly to a theory of solids which, as far as it has been tested, agrees remarkably well with the facts. I wish also to emphasize the point that the most convenient way of testing theories of the structure of the outer parts of the atom is by seeing the consequences they involve as to the properties of the elements when in the solid state. It sounds paradoxical, but it is true, that it may be less laborious to calculate the properties of practically an infinite number of atoms than of a single molecule with only two or three atoms.

The reason for this is very simple. Suppose we are considering a single molecule say of oxygen, as each atom of oxygen has six free electrons, we may regard the twelve electrons as distributed so that four are in the plane *A* bisecting at right angles the line joining the centres of the atoms. Another four are in a parallel plane *B* to the right of the two atoms, and another four in a plane *C* placed symmetrically on the left, with this distribution

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* Presented at the Stated Meeting of the Institute held Wednesday, May 17, 1922.

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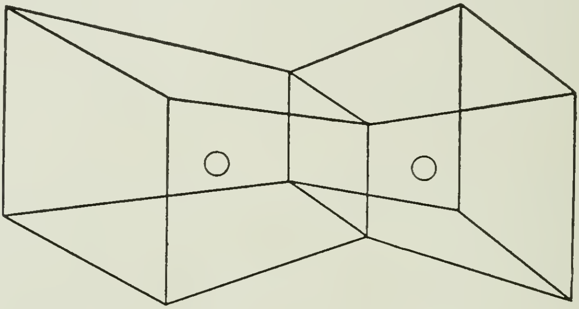
each oxygen atom may be regarded as surrounded by an octet of electrons.

Now the electrons in the plane *A* will be under different forces from those in the planes *B* and *C*. The result will be that the octets will not be cubes but figures like those in Fig. 1 whose geometry is somewhat complicated.

Now let us consider an oxygen atom in a solid crystal of oxygen, each atom will be surrounded by a symmetrical distribution of atoms and electrons and the arrangement of electrons round each atom will be quite symmetrical, so that these electrons will be on a cube instead of on the camera-shaped figure shown in Fig. 1. It is true that in the solid we have in our calculations to take into account the influence of the large number of neighbors which each atom possesses, whereas in a single molecule each atom has but one neighbor, but as a matter of fact when the atoms are, as in a crystal, regularly spaced and arranged, the difficulty of doing this is not great and is far more than counterbalanced by the simplicity gained by having to deal with symmetrical and regular bodies like cubes instead of the distorted figures of the molecule.

Fig. 1.



The solids which have the simplest constitution are crystals of the various chemical elements since in these all the atoms are of one kind. The valency of the element will have great influence upon the shape and properties of the crystals, for the crystalline shape must be such as to give the right proportion between the number of electrons and the number of atoms, and this proportion depends upon the valency of the element. Thus in a monovalent element like one of the alkali metals there is but one disposable electron for each atom; in a divalent element there are two; in a trivalent, three, and so on.

In a crystal of a monovalent element the arrangement of atoms and electrons must be such that there is one atom for each electron. Such a proportion is ensured (*a*) if the atoms *A* are placed at the centres of cubes at each corner of which there is an electron *E*, as in Fig. 2; or (*b*) as in Fig. 3, when the atoms *A* and electrons *E* are placed alternately.

In a monovalent element the positive charge on the atom is equal to the negative charge on the electron. Thus in both the arrangements (3) and (4) we have a simple distribution of electrical charges and we can without much difficulty calculate what would be the potential energy due to the forces between them, if these are supposed to vary inversely as the square of the distance. But this is not the only source of potential energy. For by Earnshaw's theorem no system can be in stable equilibrium if the only forces between the bodies are those varying as the inverse square of the distance. There must therefore be between atoms and electrons and atoms and atoms forces in addition to those varying according to this law. I have shown in several papers that if we suppose that these additional forces between atoms and electrons vary inversely as the cube of the distance, we get simple explanations of many chemical phenomena, such, for example, as valency and Mendeleeff's Periodic Law. The result of considering the consequences of the inverse cube law when applied to the theory of solids also furnishes very strong evidence in its support. For supposing that the only forces in addition to those varying inversely as the square of the distance are those forces varying as the inverse cube, we can calculate the potential energy of the crystal. I have made this calculation in a paper published in the April number of the *Philosophical Magazine*, and find that the potential energy for each atom of a monovalent element and its associated electron is when the atoms and electrons are arranged as in Fig. 2, equal to

$$-1.825\frac{e^2}{d}$$

where *d* is the distance between two atoms and *e* the charge on an electron. If M is the mass of an atom, Δ the density of the crystal will be equal to

$$\frac{M}{d^3} \text{ for } \frac{1}{d^3}$$

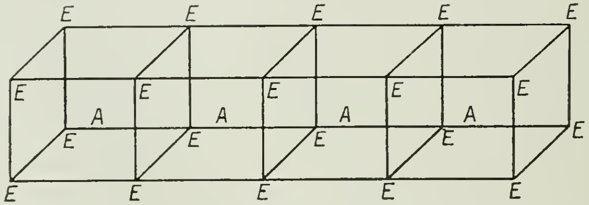
is the number of atoms per unit volume.

Thus,

$$\frac{1}{d^3} = \frac{\Delta}{M}$$

and as both M and Δ are known, the value of d is determined.

FIG. 2.



If the atoms and electrons are arranged as in Fig. 3, the energy per atom with electron is equal to

$$-.885\frac{e^2}{d'}$$

where d' is the distance between an atom and an electron and is given by

$$\frac{1}{d'^3} = \frac{2\Delta}{M}.$$

Now if we compress the solid we shall alter d, and with d the energy of the crystal. From the preceding expressions we can find the energy required to produce any specified compressions, and from this we can deduce the coefficient of compressibility of the solid. In this way I find that the bulk modulus K (which is the reciprocal of the compressibility) is given by the relation

$$K = \frac{3.65}{9}e^2\left(\frac{\Delta}{M}\right)^{\frac{4}{3}}$$

for the arrangement in Fig. 2 and by

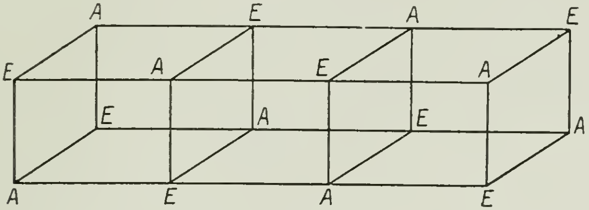
$$K = \frac{2.2}{9}e^2\left(\frac{\Delta}{M}\right)^{\frac{4}{3}}$$

for that in Fig. 3. As e and $\frac{\Delta}{M}$ are known for the different elements, we can find the value of K. The following tables contain the values of K calculated by the first of these formula and also the value found by Richards in his invaluable researches on the compressibility of the elements.

	K calculated	K found by Richards
Lithium	$.14 \times 10^{12}$	$.114 \times 10^{12}$
Sodium	$.068 \times 10^{12}$	$.065 \times 10^{12}$
Potassium	$.03 \times 10^{12}$	$.032 \times 10^{12}$
Rubidium	$.022 \times 10^{12}$	$.025 \times 10^{12}$
Cæsium	$.016 \times 10^{12}$	$.016 \times 10^{12}$

Thus we see that not only the relative values of the compressibility, but also the absolute ones, are given accurately by the expression which corresponds to the arrangement represented by Fig. 2. The values corresponding to the arrangement in Fig. 3 are little more than half these, and are ruled out of court by Richards' experiments. We conclude then that Fig. 2 represents the arrangements of atom and electrons in the alkali metals.

FIG. 3.



A further test of theory is got by considering the elements with higher valencies. Let us take first the divalent elements where there must be two disposable electrons for each atom. This necessitates an arrangement of electrons quite different from that for the alkali metals. One arrangement which gives two electrons for each atom is to place the electrons at the corners of hexagonal prisms and the atoms at the centres of the prisms. As each corner is the meeting place of six prisms the twelve electrons will only count as two, and there will be two electrons for each atom. This would give hexagonal symmetry and would involve crystallization in the hexagonal system. As a matter of fact most divalent elements do crystallize in that system. The calculation of the energy corresponding to this distribution of electrons is more complicated than that for the alkali metals, because two lengths are required to fix the hexagonal prism; *viz.*, the height and the radius of the base. This makes the numerical calculations somewhat lengthy, and I have not yet completed them. I have, however, calculated the energy for another distribution of electrons which would also give two electrons per atom, which would correspond to crystals with uniaxial symmetry, and for which the geometry is simpler. In this arrangement the atoms are at the centres of cubes, and the electrons at the corners of the cubes and at the middle points of *one* pair of parallel faces.

For this distribution I find that the potential energy per atom with two electrons is

$$-10.27\frac{e^2}{d}$$

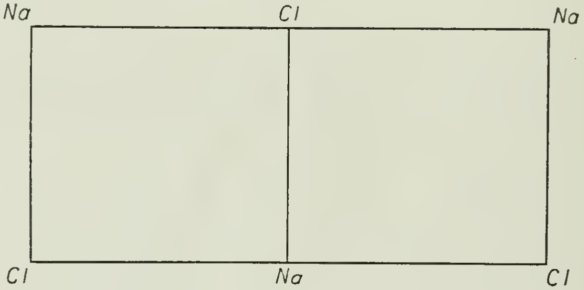
where e is the charge on an electron and d the size of the cube. If Δ is the density of the crystal and M the mass of the atom

$$\frac{1}{d}=\left(\frac{\Delta}{M}\right)^{\frac{1}{3}}$$

so that the potential energy is

$$-5.13\,e^2\left(\frac{\Delta}{M}\right)^{\frac{1}{3}}.$$

Fig. 4



It follows from this that K, the bulk modulus, is given by the equation

$$K=\frac{10.26}{9}\,e^2\left(\frac{\Delta}{M}\right)^{\frac{4}{3}}.$$

The values of K, calculated from this expression, and the values found by Professor Richards, for the divalent element, are given in the following table

	K calculated	K observed
Magnesium	$.408 \times 10^{12}$	$.378 \times 10^{12}$
Calcium	$.185 \times 10^{12}$	$.182 \times 10^{12}$
Zinc	$.72 \times 10^{12}$	$.67 \times 10^{12}$
Cadmium	$.45 \times 10^{12}$	$.53 \times 10^{12}$

Let us now consider the trivalent elements; for these there are three electrons per atom. There are several ways in which the electrons might be arranged which would correspond to different systems of crystallization. The arrangement corresponding to the cubical form is when the atoms are placed at the centres of regular dodecahedra with the electrons at the corners. Space can be packed with these dodecahedra, and when this is done each of the six four-edged corners of a dodecahedra is the meeting place of six dodecahedra, while each of the eight three-sided corners is the meeting place of four; thus the six four-edged corners count as one and the eight three-edged as two, and, therefore, the fourteen corners of the dodecahedra as three.

We can show that when dodecahedra are packed in this way the centres are arranged like a system of face-centred cubes; the electrons are at the middle points of the sides of these cubes and also at the centres of the eight smaller cubes into which a cube is divided by planes bisecting its sides at right angles.

I have calculated the potential energy per atom and their electrons for this arrangement and find that it is equal to

$$-14.4\,\frac{e^2}{4^{\frac{1}{3}}}\left(\frac{\Delta}{M}\right)^{\frac{1}{3}}$$

and the bulk modulus is

$$\frac{28.8}{9}\,\frac{e^2}{4^{\frac{1}{3}}}\left(\frac{\Delta}{M}\right)^{\frac{4}{3}}$$

where Δ is the density of the crystal and M the mass of the atom. Aluminium is a trivalent element crystallizing in the regular system, for which $\frac{\Delta}{M}$ is

$$\frac{2.65}{27}\times\frac{1}{6.4\times 10^{-24}}.$$

Substituting this value we find the bulk modulus to be $.98\times 10^{12}$, the value found by experiments is $.78\times 10^{12}$.

For quadrivalent elements there must be four electrons for each atom. The arrangement which would give this proportion and produce crystals belonging to the regular system is when the atoms are at the centres of cubes and the electrons at the corners and middle points of all the faces of the cube.

I have shown[1] that the potential energy per atom with four electrons is equal to

$$-16.67\ e^2\left(\frac{\Delta}{M}\right)^{\frac{1}{3}}$$

and that the bulk modulus is equal to

$$\frac{33.35}{9}\ e^2\left(\frac{\Delta}{M}\right)^{\frac{4}{3}}.$$

The diamond crystallizes in the regular system, for it $\Delta = 3.52$. This would make the bulk modulus for the diamond 8.1×10^{12}; this is very much higher than the value 2×10^{12} obtained by Richards. This difference suggests that the unit in the case of the diamond is a group of three or four atoms and not a single atom. We see from the preceding investigation that whatever be the valency of the element the expression for the bulk modulus contains the factor $\left(\frac{\Delta}{M}\right)^{\frac{4}{3}}$; the other factor depends only on the valency and increases as that increases.

The expressions for the potential energy of an atom with its associated electrons given above are for atoms in the body of the crystal; for atoms at the surface the potential energy will be greater. Suppose that βE is the excess of an atom at the surface over the energy E possessed by an atom in the interior. If d be the distance between the atoms, the number of atoms per unit area of surface is $\frac{1}{d^2}$, so that the excess of energy possessed by unit area of surface is $\frac{\beta E}{d^2}$, and this must equal to T the surface tension; hence since, as we have seen, E varies as $\frac{1}{d}$

$$T = \frac{\beta'}{d^3}$$

where β' is a constant proportional to β and depending upon the valency. But K, the bulk modulus $= \frac{y}{d^4}$, where y is quantity, depends on the valency, thus

$$T = \beta'\ \frac{k^{\frac{8}{4}}}{y}.$$

For substances of similar constitutions both β' and y will have the same values; hence for such substances T will be proportioned to $K^{\frac{3}{4}}$. This relation was dicovered by Richards.

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[1] *Philosophical Magazine*, April, 1922.

Hitherto we have confined our attention to elementary substances; similar principles will also apply to compounds, though for these the calculation of the potential energy is much more complicated. The reason for this is that when the atoms are different the distribution of electrons round one kind of atom need not be the same as that round the other kind. Thus, take NaCl as an example; there are eight electrons for each molecule of the salt. If the atoms of Na and Cl are arranged alternately as in Fig. 4, one way of disposing of the electrons would be to place them at the corners of cubes whose centres are at the chlorine atoms and whose sides are parallel to the lines of the space lattice formed by the sodium and chlorine atoms. With this arrangement the crystals would belong to the regular system. The measure of its physical properties would depend upon the dimensions of the cube of electrons round the chlorine atoms. If the side of this cube is small compared with the distance between the atoms of sodium and chlorine, we can prove without difficulty that the expression for the bulk modules would be the same as given for the arrangement Fig. 3 for a monovalent element, the bulk modulus calculated on this assumption would be much less than the value found by Richards for NaCl. If we go to the other extreme and suppose that the cube round the Cl atom extends half-way to the Na atom, the electrons will be arranged as face-centred cubes and the expression for the energy and bulk modulus will be that given for a quadrivalent element. The bulk modulus calculated in this way is much greater than that found by Richards; thus for some dimensions of the cube intermediate between these values the calculated value of the bulk modulus will agree with that found by Richards. If we know the intensities of the forces varying inversely as the cube of the distance, we can calculate the dimension of the cube of electrons, the calculation is, however, somewhat lengthy, and I must leave it for another occasion. I may remark, however, that Richards' result for the halides of the alkali metals show that these are in very fair agreement with the general result that for similar bodies the bulk modulus is proportional to $\left(\frac{\triangle}{M}\right)^{\frac{4}{3}}$.

An Alcohol Problem.—At the last meeting of the Association of Official Agricultural Chemists, a discussion was held in regard to the respective advantages of the tables published by the Association and those recognized by the United States Pharmacopeia. The A.O.A.C.

tables are based on the Bureau of Standards data 20°/4°, and represent true specific gravities, whereas the U. S. P. tables are based on the Bureau of Standards tables 15.56°/15.56°, and represent apparent specific gravity of 750 millimetres and 50 per cent. air saturation. The A. O. A. C. tables are favored from a purely scientific point of view, but trade considerations in an industry so intricate in its public relations cannot be overlooked. Sixty degrees/sixty degrees F. is written into the United States Revenue law. The question of temperature is important only in the case of per cent. by volume. The A. O. A. C. rules which require specific gravity refractive index and rotation to be determined at 20° make for uniformity. An expression of opinion by those interested in the matter is desired. Such opinion should be transmitted to L. F. Kebler, Chairman, Washington, D. C.

H. L.

Chemical Studies of Swimming-pool Water.—ROY W. GOSHORN, of the Hahnemann Medical College of Philadelphia (*Hahnemannian Monthly*, 1922, lvii, 460–469), has examined the water from five swimming pools in Philadelphia; one pool was used exclusively by women, two pools exclusively by men, and two pools by both sexes. From six to fifteen samples were taken from each pool at definite intervals of time; determination was made of the concentration of chlorides, nitrogen as free ammonia, nitrogen as nitrates, nitrogen as nitrites, and nitrogen as urea in each sample. The treatment of the water and the number of people using the pool between analyses were also noted. The contamination of the water was greatest in the pool used only by women, and least in the pools used only by men; pools used by both sexes occupied an intermediate position with respect to contamination. These findings were based on the concentration of urea, nitrates, nitrites, and free ammonia in the respective groups of pools. Treatment of the water with cupric sulphate apparently had no influence upon its chloride and nitrate content.

J. S. H.

Sealing Quartz to Glass.—E. O. HULBURT, of Iowa State University (*Science*, 1922, lvi, 147), recommends the use of silver chloride for sealing quartz to glass. For example, the end of a glass tube was ground evenly, warmed to a temperature above 500° C. in a Bunsen flame and quickly dipped into powdered silver chloride. The silver chloride, which adhered to the glass tube, was melted by further heating. The tube was secured in an upright position; the plate of quartz was placed on top of it; and heat was applied until the silver chloride melted and made optical contact with the plate. Fused quartz plates fractured less frequently than plates cut from quartz crystals, hence were preferable. Glass tubing with a wall of medium thickness stood the strain best after sealing had been accomplished.

J. S. H.

BRIDGES OLD AND NEW.*

BY

RALPH MODJESKI, C.E., D.ENG.
Franklin Medalist, Member of the Institute.

From the beginning of history, and no doubt many centuries before, the means of transportation seem to have been considered the most important factor in the progress of civilization. In his history of the Great Highways of the Roman Empire, Bergier says:

"The Rulers of the various countries took great care to maintain the highways in such condition that the people could traverse them with security and convenience; the Kings of Sparta were especially charged to see to the good condition of the roads; Augustus, elected the curator of the great highways in the vicinity of Rome, engaged as helpers persons of pretorian dignity; in France, the King, in the early times, had reserved for himself the superintendence of the great highways; he delegated the carrying out of this supervision to his 'Grand Voyer'; Henry IV appointed as 'Grand Voyer' his Prime Minister Sully, that is, the man whom he esteemed most."

The existing records of ancient bridges, meagre as they are, seem to indicate that men were building bridges at least sixty centuries ago.

We do not know exactly when one type of bridge followed another; but it is certain that all our modern types, such as girder, arch, suspension, and even cantilever, were used in primitive shape in those very ancient times. We have still existing examples of the beam or girder bridge; monuments proving age-old knowledge of a rudimentary arch; we have records of the early use of the suspension type; and records of the cantilever combined with the girder type connecting-span almost challenging our credulity.

The first bridge built by man no doubt was of the kind easiest to build—possibly a tree thrown across a stream or ravine. Thus unwittingly, the man invented the girder. But as early as 4000 B.C., notable progress must have been achieved in the art of bridge-building, for, according to Herodotus, Menes, one of the first Kings of Egypt, then had a bridge constructed over a branch of the Nile and though we have no details of this early structure it must have consisted of at least several girders or even arches.

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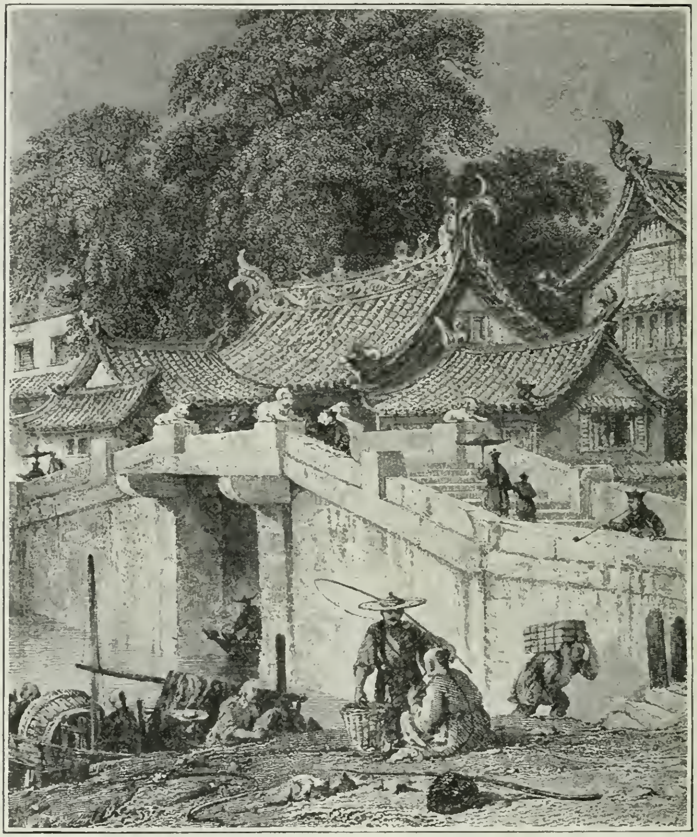
* Presented at the Stated Meeting of the Institute held Wednesday, May 17, 1922.

FIG. 1.



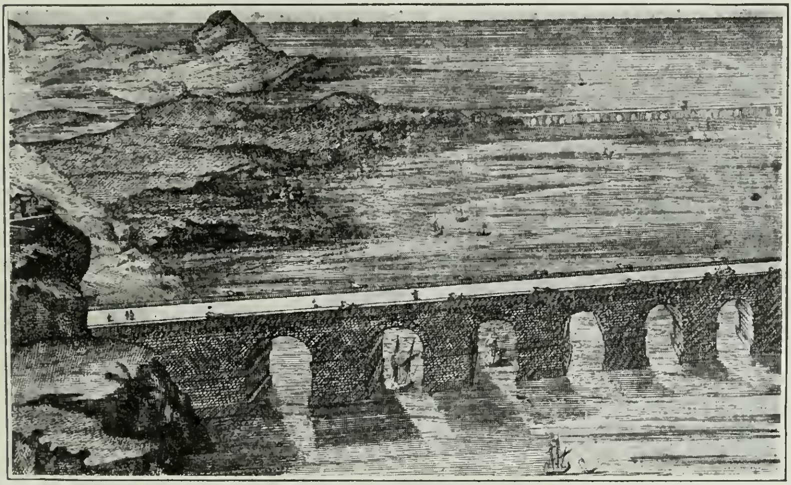
Slab bridge at Chapoo, China.

We have mention in history of Lake Villages in the Bronze Age, or about 1400 to 1200 B.C. They consisted of many bridges built of wood leading to a central group of dwellings. There are remains of a Lake Village in Glastonburg in the British Isles.

LINTEL AND SLAB BRIDGES.

Among the oldest monuments we have of bridge construction are the so-called lintel and slab bridges. The former consisted of oblong stones placed vertically in the stream and spanned by long, flat, narrow stones or lintels. Sometimes lintels have been placed on piers built of smaller stones. There are some examples of these ancient bridges in the Valley of Wycoller in Lancashire, England, dating back to the Bronze Age. The so-called slab bridges differed from the lintel bridges in that large slabs of stone were used instead of narrow ones. Some examples still exist in the Dartmoor region, England. But it is China, probably, who has built more slab bridges than all other countries combined. There, as in other countries, a single-span bridge—arch or beam—was the first form constructed. Such is the type of the bridge at Chapoo which is very ancient though information even as to its approximate age has not been found. It is a bridge for pedestrians only, built of stone slab beams resting on stone abutments; most beautifully proportioned as a whole and in all its parts (Fig. 1). There are many similar single-span bridges in China of more or less ancient origin, all of them showing the extraordinary ability and workmanship of their builders.

FIG. 2.

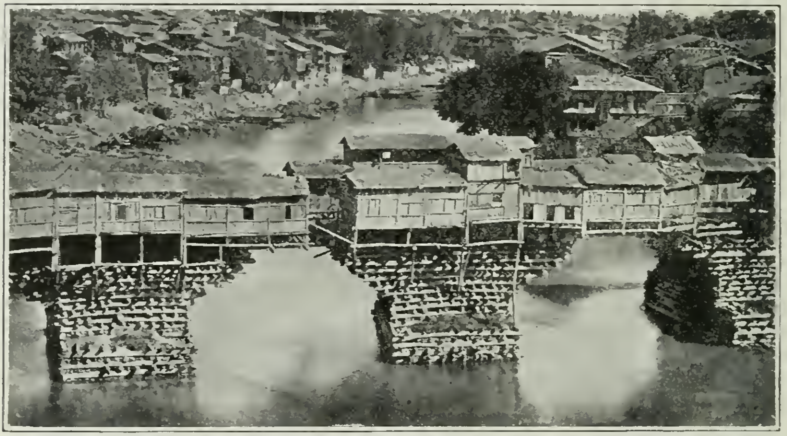


Bridge at Fo-Cheu, China.

CHINESE ARCH BRIDGES.

Later, with the advance of civilization, bridges of greater length—of more spans—made their appearance. Emiland Gauthey speaks of a bridge, said to be still in existence, at Loyang, in the province of Fo-Kien, which has three hundred spans; it took eighteen years to build it, and five thousand men were employed. It is probably a slab bridge. The slabs are said to be of huge dimensions: about 9 feet by 15 feet by 100 feet. Gauthey further expresses a doubt as to the correctness of these dimensions and according to Pingeron they are only about 4½ feet by 4½ feet by 45 feet. Even then, Gauthey says: "It is a wonderful achievement—more than four and a half times longer than the Pont Saint Esprit." Taking the dimensions given by Pingeron, the bridge is about 14,500 feet long. It is ornamented by large marble lions, a decoration which has often been used in the old Chinese bridges. It is again Gauthey who describes a bridge of 24,000 feet in length in the province of Fo-Cheu, over the river Min. It is said to have a hundred arches, all semicircular, of an average opening of 128 feet, and a width of 60 feet. The piers, therefore, are very broad, and the height is 120 feet. This bridge also is ornamented with huge lions in black marble cut out of blocks twenty-two feet long. It was said of this bridge that vessels could pass under the arches with all sails set (Fig. 2).

FIG. 3.



Bridge at Srinegar, India.

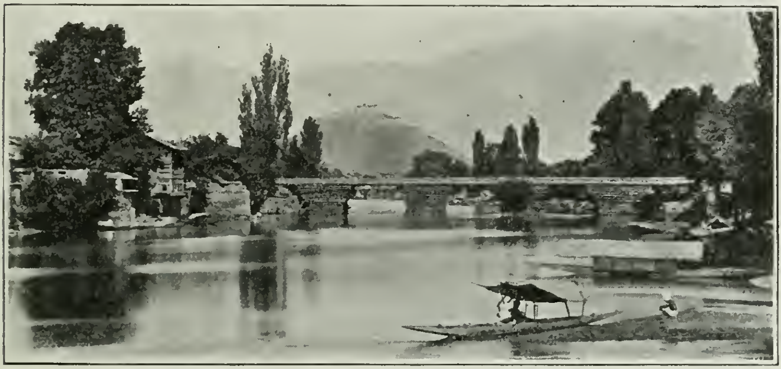
PRIMITIVE CANTILEVER BRIDGES.

However it may stand between the wooden and the stone span as to priority in history, there came a time when the two materials were combined in the construction of bridges.

The Lake Village bridges were apparently all of wood while the lintel and slab bridges were of stone; both these types, as said before, dating back to the Bronze Age.

But Violet le Due found in Savoy (France) a primeval bridge built of logs laid criss-cross, each layer of logs projecting beyond the one below and the crib thus formed filled with rock. These cribs then had the shape of brackets or cantilever arms projecting over the stream. The gap between them was bridged with timber. Here we have a prototype of the cantilever bridge. Criss-cross bridges of several spans may still be found in use in Kashmir, India, and in other eastern countries.

FIG. 4.



Bridge at Srinegar, India.

The bridges at Srinegar, India, built of deodar logs, are typical examples of this kind of construction; they have several piers, each corbeling towards its neighbors, the remaining spaces being bridged over by long beams (Figs. 3 and 4).

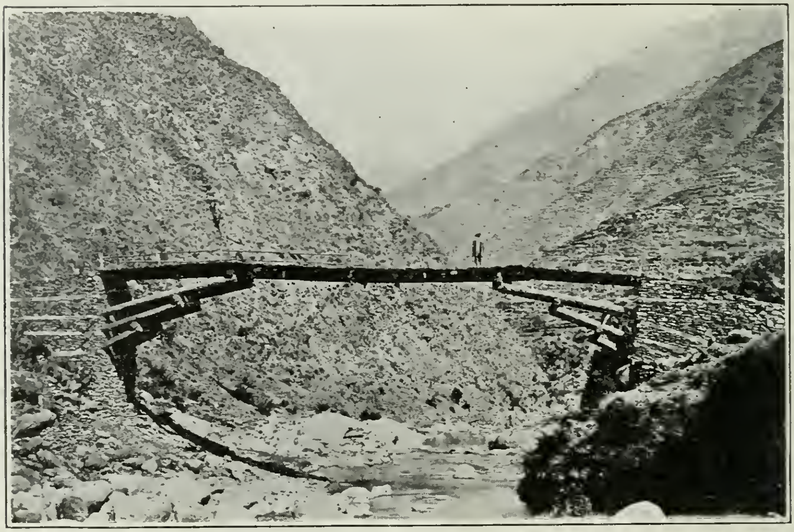
One of these bridges has houses or shops built closely side by side over the whole length of it. This idea has been repeated often in European bridges; as in the well-known old London Bridge, the Ponte Vecchio in Florence, and in certain old Swiss bridges. The merchants evidently selected a location where passing their shops was unavoidable.

A still nearer approach to the true cantilever is seen in the primitive form in the bridge near Darjeeling, in the Himalaya Mountains, N. W. India (Fig. 5).

LEGENDARY BRIDGES.

Herodotus mentions that a magnificent bridge was built over the Euphrates at Babylon. This bridge is said to have had stone piers connected by planking which was removed at night. As building foundations under water was not known, the river was diverted during the construction of the piers. Diodorus ascribes the bridge to Semiramis, which would place it nearly 800 B.C. There is an historical mention of large pontoon bridges built by Darius on the Danube about 500 B.C. and somewhat later one by Xerxes on the Hellespont, but unfortunately no details of the construction of these various structures have reached us.

FIG. 5.



Bridge near Darjeeling, India.

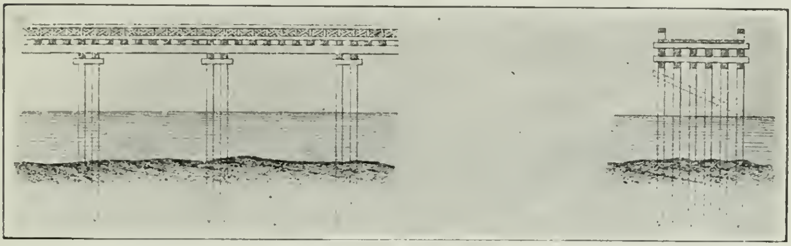
FIRST ROMAN BRIDGES.

To the Romans is due the greatest progress in bridge-building. They did not hesitate to cross the broadest streams in their march to conquest and did so by means of various types of structures—

wooden trestles, wooden arches on stone piers, or with purely stone arches.

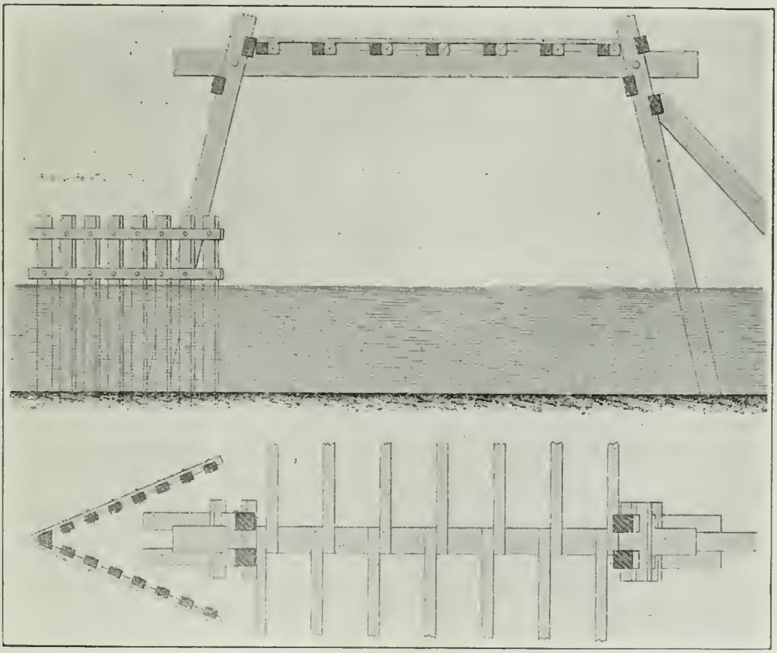
The Roman aqueducts, built about 600 B.C., consist of masonry arches, but the opening of the arches never exceeded 20 feet.

FIG. 6.



Pons Sublicius.

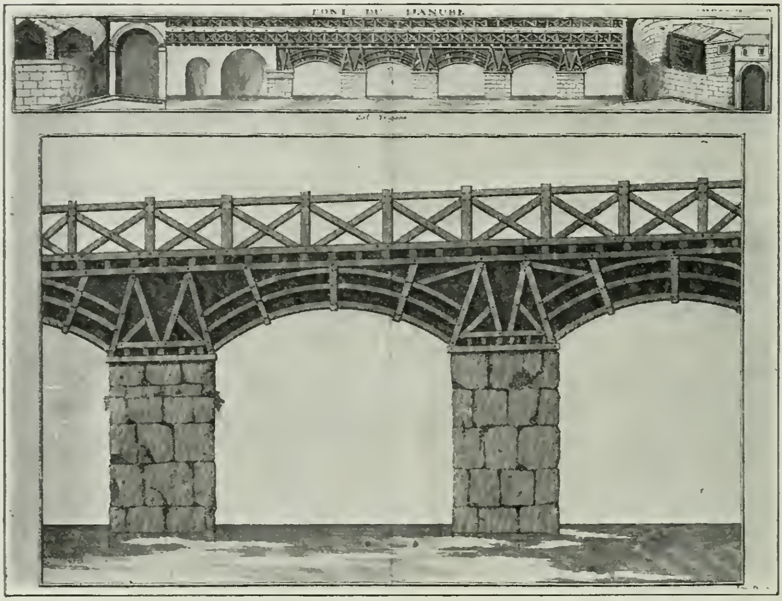
FIG. 7.



Bridge over the Rhine, built by Caesar.

The first Roman bridge of which we know was built of timber in 620 B.C., at the foot of the Aventino Mountain. It was called Pons Sublicius. There is some controversy as to its exact location on the Tiber. It was built entirely of wood, not unlike our modern trestles (Fig. 6). According to Denis of Halicarnassus, this bridge was built at the expense and by the efforts of the first religious heads, whence their name "Pontifices." It was destroyed in 507 B.C., while Horatius Cocles was defending its passage. Pliny says that in rebuilding it care was taken not to use any iron or nails, to facilitate its destruction in future wars.

FIG. 8.

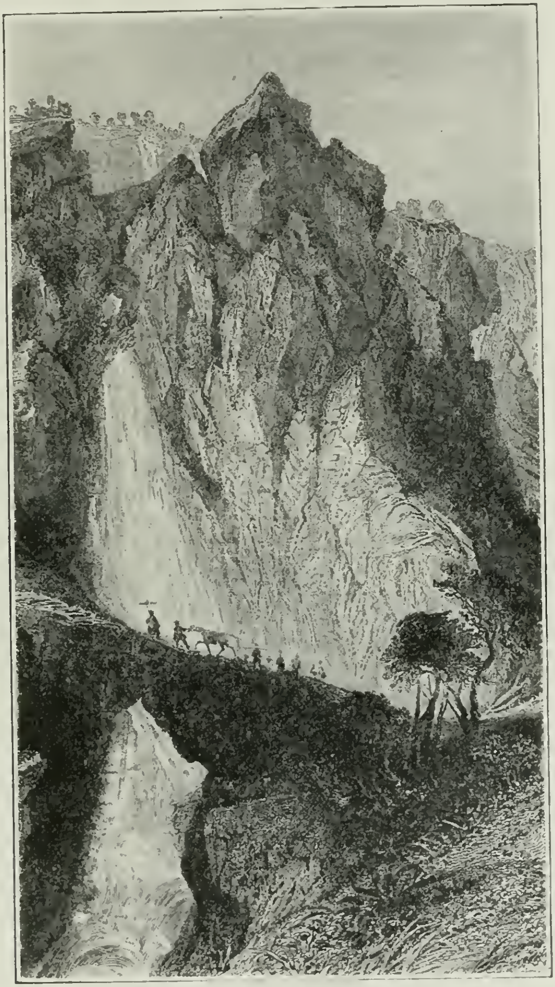


Trajan's Bridge over the Danube.

History speaks of a timber bridge built over the Rhine by Cæsar in 55 B.C. It was temporary and simple, but said to be very solid. It was from 2000 to 2300 feet in length, and is said to have been built in ten days (Fig. 7).

Trajan was a great bridge builder. His bridge over the Danube just below the Iron Gate was in his time a gigantic undertaking. It was built probably about 104 A.D. (Fig. 8). Its engineer was Apollodorus of Damascus, who also built the Trajan Column in Rome, on which there is a bas-relief of the bridge apparently distorted by the sculptor. The ancient historian, Dion Cassius, states that the bridge had twenty piers of hewn stone, 150 feet high and 60 feet wide, with openings between them of 170 feet. The bas-relief gives clear information that the stone piers were connected by wooden arches. There are still thirteen piers visible out of the twenty. The length of this remarkable structure is said to have been 3900 feet (Murray's Handbook),

FIG. 9.



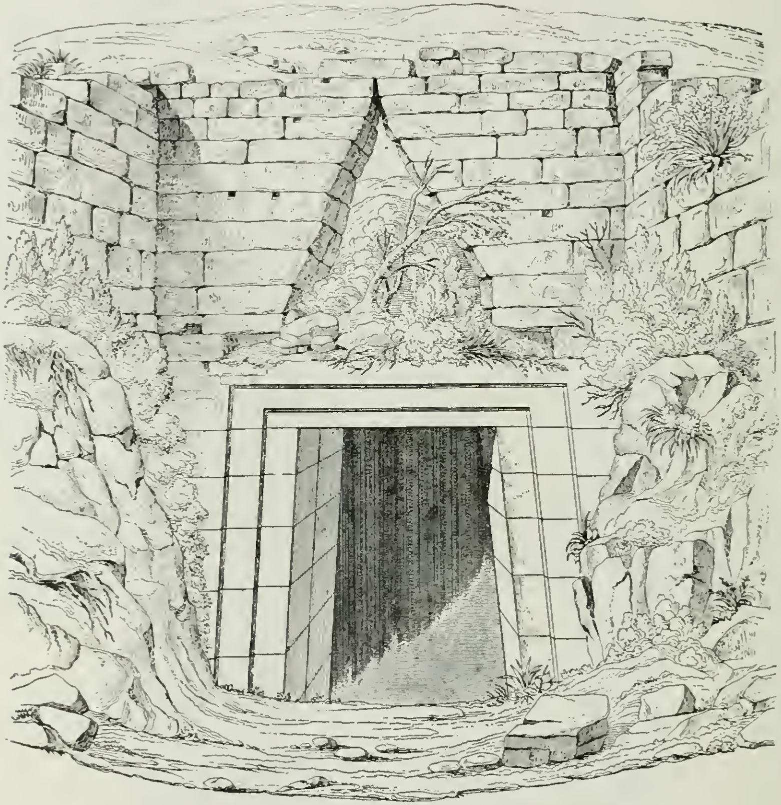
Natural bridge at Han-tseuen, China.

although other sources give this length as nearer 3000 feet. It is believed that the foundations for the piers were obtained by sinking caissons.

FIRST STONE ARCHES.

The true stone arch came to be used only after other forms of construction resembling the arch had been tried. In fact, there seems to have been a definite process of evolution and its different stages are quite marked. No doubt the first idea of an arch came to man from some natural rock formations of which there are many throughout the world. One of the most remarkable instances, and where this natural bridge is used as a crossing, is at Han-tseuen, in the Province of Kiang-nan, China (Fig. 9).

FIG. 10.

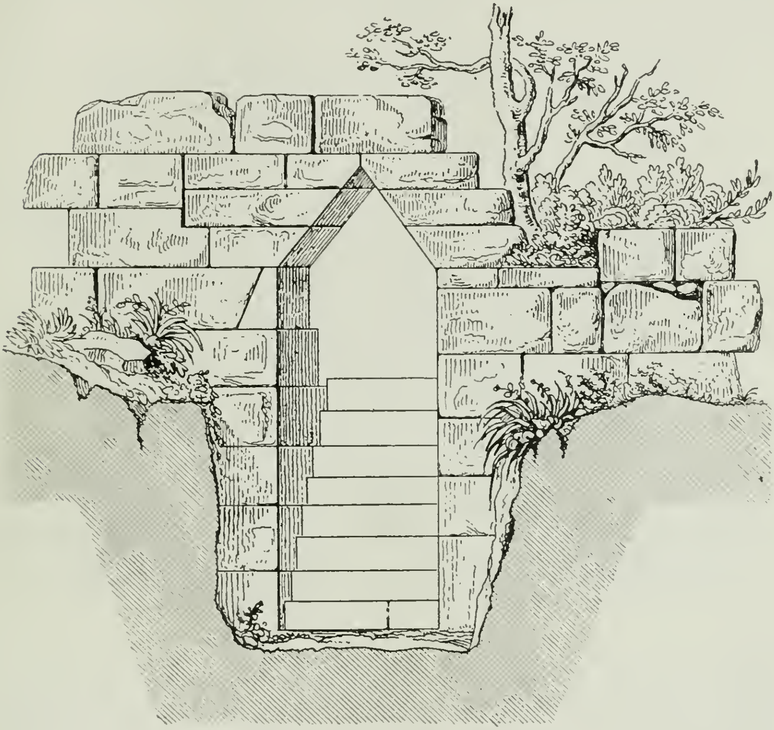


Agamemnon's Grave at Mycenæ.

But, being monoliths, these natural arches gave no indication of how to imitate them with smaller stones, so that the arrangement of joints became the subject of experiment through many centuries.

The Egyptians and the Greeks built arches in very ancient monuments, but they were not true arches and had only very small openings. In Greece, especially, the first arches were built of stones laid in horizontal courses, each course projecting beyond the one below. This was first done cautiously, so that the top courses did not meet as in the later constructions but the remaining space was bridged by a lintel. An example of this endeavor to approach an arch is seen in the entrance to the commonly called Agamemnon's grave at Mycenæ (Fig. 10). The lintel still exists but the horizontal courses supporting it approach each other as they rise. The upper triangular opening shown in the cut

FIG. 11.

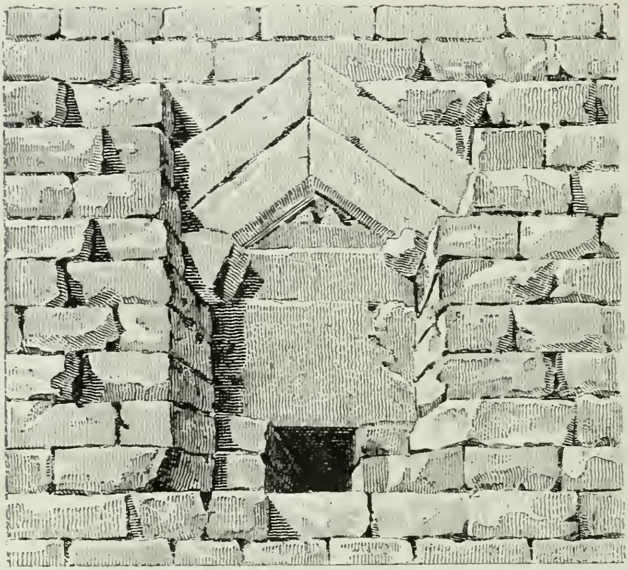


Entrance to theatre at Messina.

must have been filled by some ornamental slab which was subsequently removed. It is even possible that this was done to relieve the weight on the lintel. In the entrance to the theatre at Messina, Greece, the lintel is omitted and the approach to the arch becomes closer (Fig. 11).

But the real prototype of the true arch, where the stability depends entirely on abutment resistance to horizontal thrust, is found in the entrance to the great pyramid at Memphis (Fig. 12); also in the roof of a granite grotto of cyclopean masonry, situated on the Island of Delos near the top of the Acropolis (Fig. 13).

FIG. 12.



Entrance to the great pyramid at Memphis.

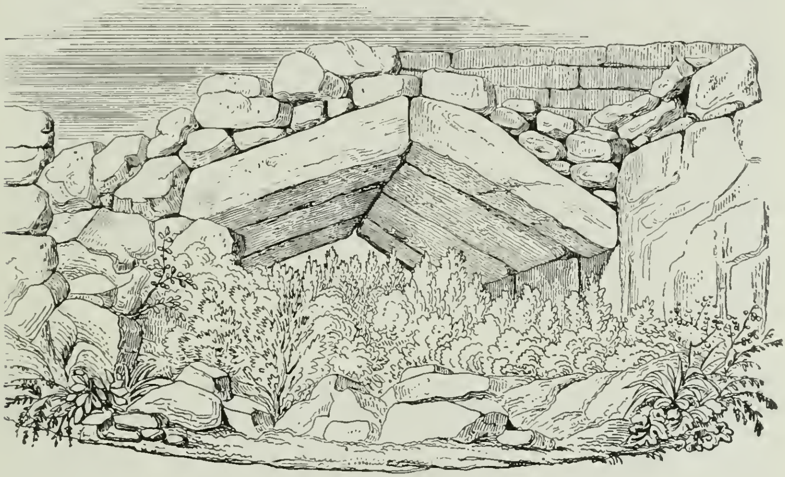
ROMAN STONE ARCH BRIDGES AND AQUEDUCTS.

Gauthey says that Pons Salaro over the Treverone in Rome was built 600 years B.C. It is not known if it was built of stone at that time or merely of wood and replaced by stone arches later. It appears to have been a stone arch bridge by the year 361 B.C. In any event, it is probably the earliest Roman stone arch bridge. It consisted of five arches of openings varying from 22 to 69 feet. Pons Palatinus, built in 179 B.C., is now known as Ponte Rotto. One arch is still in existence.

The Romans built many stone arch bridges during the beginning of the Christian era, many of which have been partly or wholly preserved, and some of which are even still in use. The Rimini Bridge (Fig. 14), built under Augustus, is perfectly preserved. The Pons Aelius, now Saint Ange, built about 130 A.D. by Emperor Hadrian, has been repaired and ornamented with statues, but is entirely preserved (Fig. 15).

Only one arch of the bridge at Narni, Italy, built by Augustus Cæsar, remains standing, where originally there were four, of white marble, elaborately designed (Fig. 16).

FIG. 13.



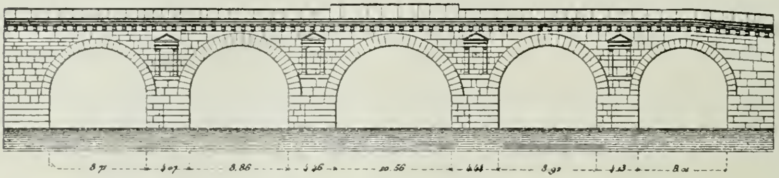
Roof of grotto at Delos.

The aqueduct of Gard in France, built by Agrippa at the beginning of the Christian era to bring water to the city of Nimes from a distance of about 24 miles, was built entirely of cut stone, 158 feet above the surface of the water. No cement or mortar was used except in the uppermost arches and as a lining in the water-carrying trough. This bridge of Gard (aside from that of Metz) is the only one which remains in France of those constructed before the twelfth century, all others having been destroyed by the invading Barbaric hordes of that period. Even this structure did not escape unharmed, both its ends having been destroyed (Fig. 17).

Of the Roman bridges still preserved in Spain, we should mention the Alcantara and the St. Martin bridges. Both of these are due to Trajan and both are very bold and remarkable structures (Figs. 18 and 19).

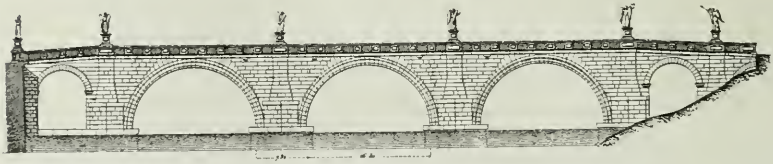
The gigantic aqueduct of Metz, of which ruins still remain, is another example of Roman enterprise, energy and ability in building great structures. This aqueduct formed a part of a very elaborate water supply system. The water of the streams was gathered into reservoirs from which it flowed through stone-lined tunnels, " so spacious that a man could walk through them with very little stooping," and crossed the Moselle on this viaduct. From there the water flowed through similar tunnels into the baths and into the Naumachia (Fig. 20).

FIG. 14.



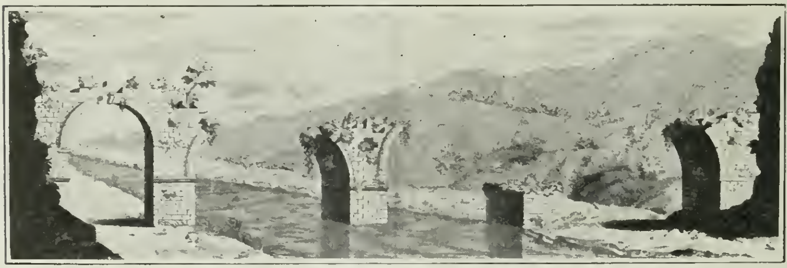
Ponte Rimini, Italy.

FIG. 15.



Pons Aelius, now Saint Ange, Italy.

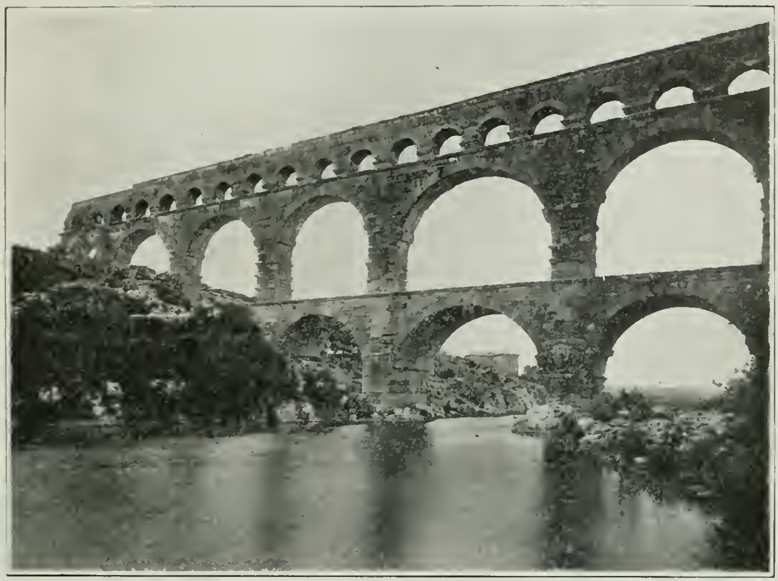
FIG. 16.



Bridge at Narni, Italy.

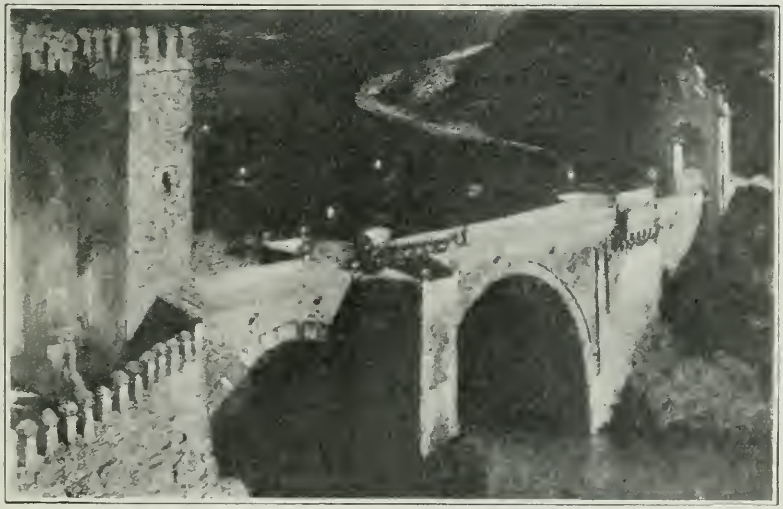
Colmenares in his history of Segovia says, that the Roman

FIG. 17.



The aqueduct of Gard, France.

FIG. 18.



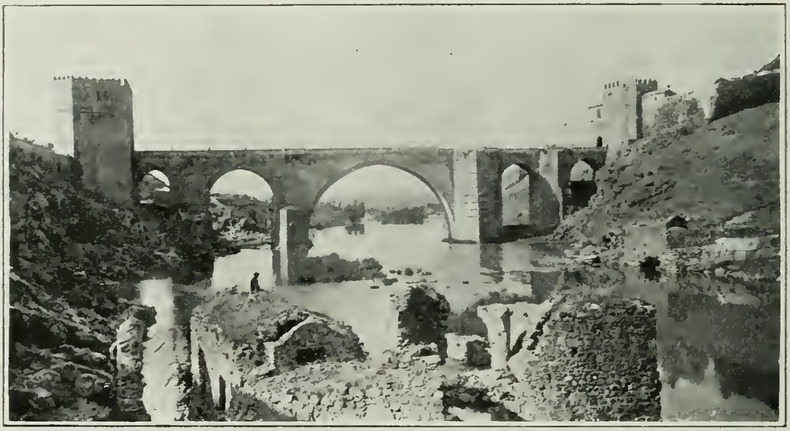
Alcantara Bridge, Spain.

aqueduct at Segovia may be cited as one of the most marvellous works left us by antiquity. Montfaucon wrote in 1722 that one hundred fifty-nine arches were still standing, all of large stones without cement. The total height was 102 feet with a double row of arches, one over the other.

Another Roman stone aqueduct is situated in Tarragone, Spain, and is very well preserved (Fig. 21).

The Romans used also brick and concrete in the construction of their aqueducts. Several ruins of this method of construction still may be seen in Italy. The one named after Nero was built of brick and was of very fine workmanship. The Alexandrine viaduct was built of brick over concrete.[1]

FIG. 19.



St. Martin Bridge, Spain.

MEDIÆVAL BRIDGES.

The Middle Ages have left us a number of bridges in various states of preservation. They are almost entirely of stone construction—arches and piers. And almost all the bridges of the twelfth and thirteenth centuries were very narrow with very steep approach grades. Often the entire absence of parapets made it very dangerous to cross them at night. There is a feeling of difference between the points of view of the builders of the Roman times and of the Middle Ages, in spite of a common quality of

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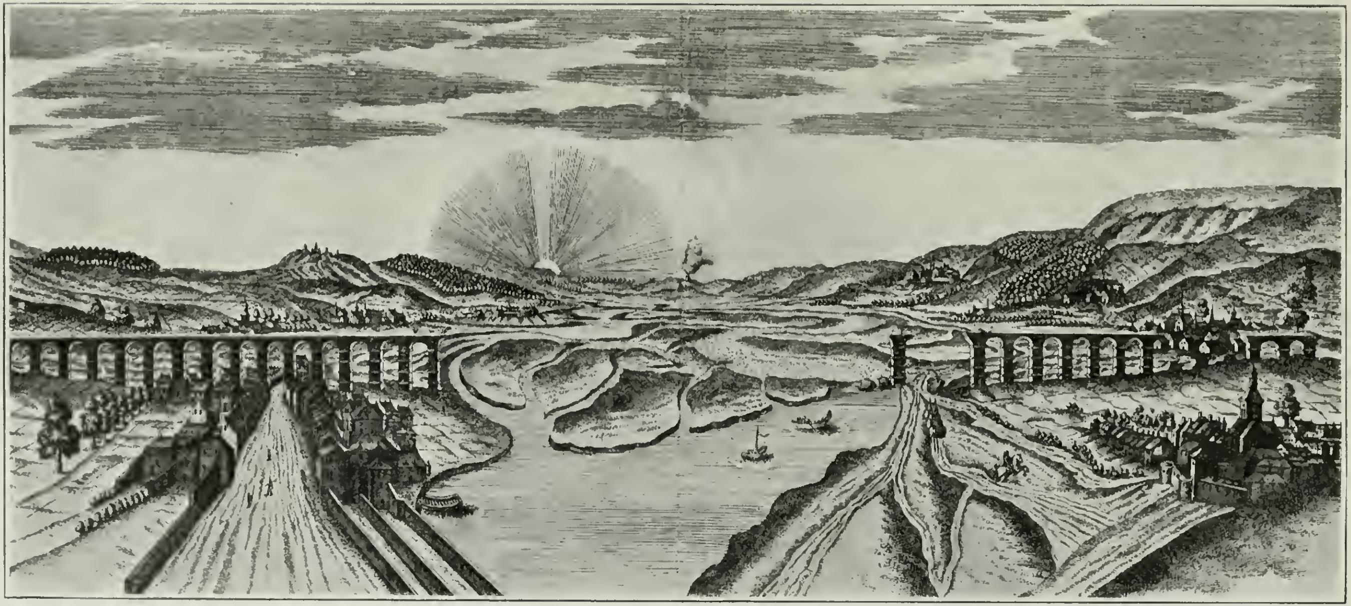
[1] W. Shaw Sparrow: "Book of Bridges."

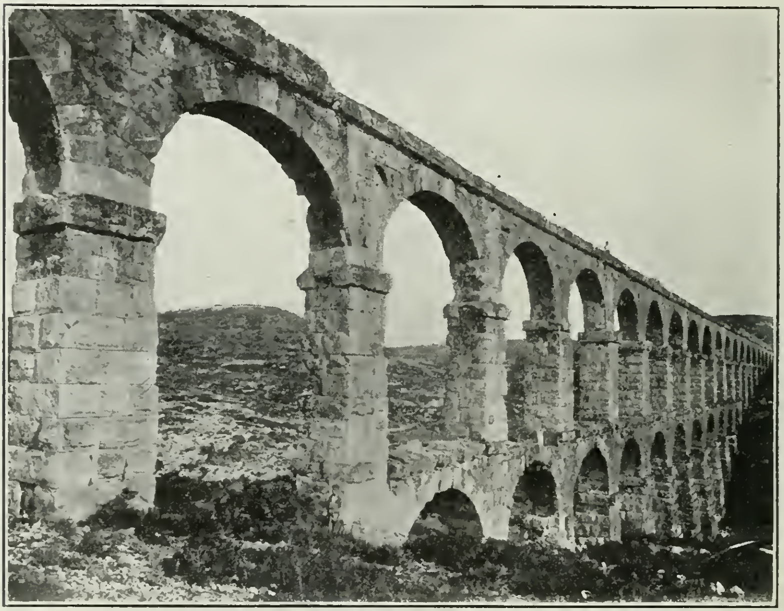
FIG. 20.



Roman aqueduct at Metz.

simplicity. The old Roman bridges seem to have been built with every line, mass and form shaped directly to meet the requirements of utility; with the result that no line or form could be questioned by the eye. But in the mediæval bridges good proportions often are hurt by a conforming to mathematical orderliness; or dignity and simplicity seem more a superficial expression of taste on the part of the monastic orders that built them.

FIG. 21.



Roman aqueduct at Tarragone, Spain.

One of the most remarkable works of those times was the Pont d'Avignon in France, built in 1178 by St. Benezet. There were twenty-one arches though to-day only four remain. The total length of the bridge was 2000 feet and the principal arches had an opening of 108 feet. St. Benezet gave his arches the form approaching an ellipse with its long axis placed vertically. This was quite a bold departure from the arches of the Romans who seemed to have used circular curves exclusively.

Over the Rhone we have the Saint Esprit Bridge, which was begun in 1265. It is said to be one of the longest stone bridges in the world and was very solidly built and strong. Its building lasted forty-five years, being finished in 1309. It was at first planned only for pedestrians and cattle, but at the beginning of the last century it was placed in service for vehicles (Fig. 22).

The Pont de la Guillotiere, also in France, is in use at present. It has been widened lately by the addition of steel arches on both sides of the bridge, resting on the old piers.

Bridges are and have been at all times the most vulnerable part of a nation's transportation system. In case of war they are the first points to be attacked and destroyed. This was plainly recognized in the Middle Ages, for most of the bridges of that time were fortified. Some conspicuous examples of such structures have been preserved. The Pont des Trous in Tournai, Belgium, for example, is protected at each end by a large tower and the parapets are high like fortress walls and provided with nine arrow-slits. Recently this bridge was again the scene of bitter struggle, when the Prussians forced a passage there (Fig. 23).

At Valentré, France, we have another example of the fortified bridge. It was built in the thirteenth century and in design has much of the grace and simplicity of the older bridges. Each of the three towers forms a vaulted passage, which could be closed by barricades when necessary. This bridge was built of small-sized stones cemented together with a mortar which has become very hard (Fig. 24).

The bridge at Orthez in the French Pyrenees, built in the twelfth century, has only one tall tower. The weight of this tower has been utilized, with Roman directness, to resist the horizontal thrust of the larger arch, being placed over the pier between the two small arches and the large one. History

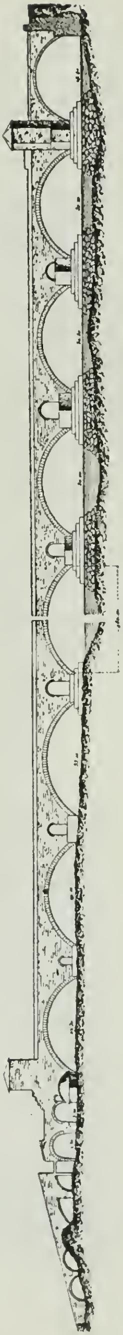
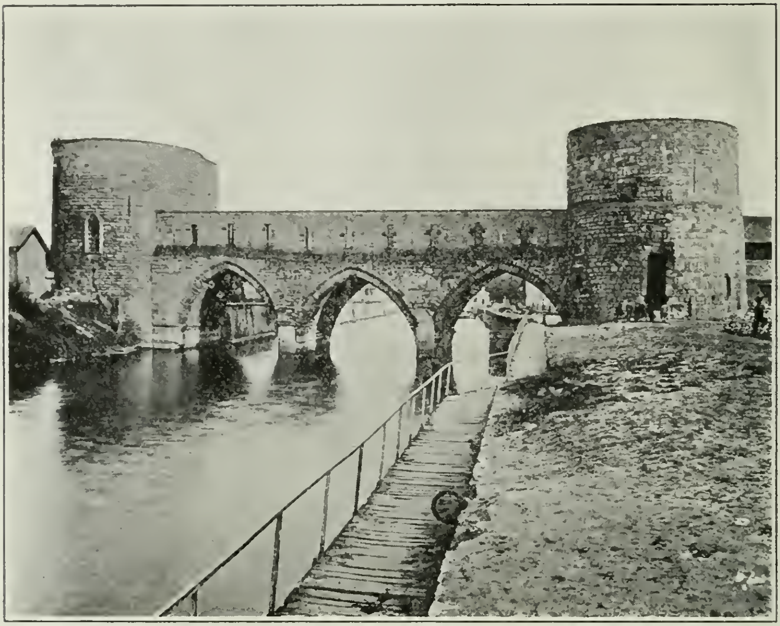


FIG. 22.

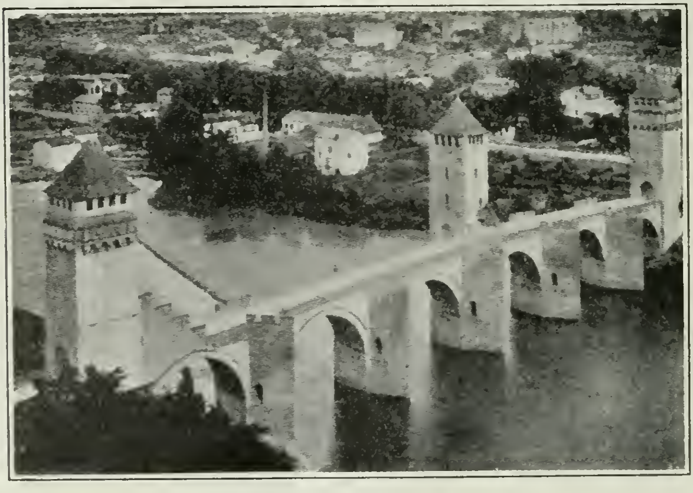
Pont du Saint Esprit.

FIG. 23.



Pont des Trous at Tournai.

FIG. 24.

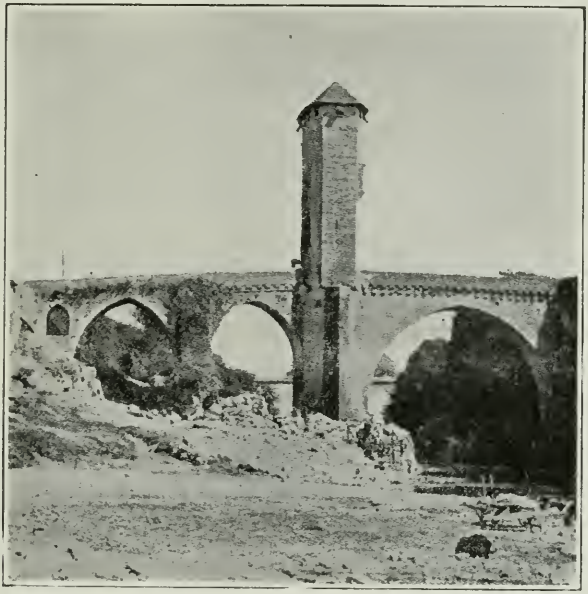


Port Valentré, France.

connects it with the battle of February, 1814, when Wellington defeated the French near Toulouse (Fig. 25).[2]

The bridge called Castelvecchio, at Verona, is a strange example of the fortified bridges, its distinctive battlements forming the parapets giving it an outline of unique picturesqueness. It was built in 1356. The base of the piers is built of white and red marble for about 12 feet above the ordinary water level. The arch wings are of limestone and the rest of brick. It is said that some of the marble was taken from Roman ruins (Fig. 26).

FIG. 25.



Pont d'Orthez, France.

One of the most interesting bridges, due partly to the Romans and partly to the Middle Ages, is the Devil's Bridge at Martorell, Spain. It would seem that the bases of the piers, the abutments and the triumphal arch (not shown on cut), which are of large cut-stone masonry, are of Roman origin, while the arches and spandril walls, which are of small stones, date from the Middle Ages. Some of its arches have a curious Gothic form

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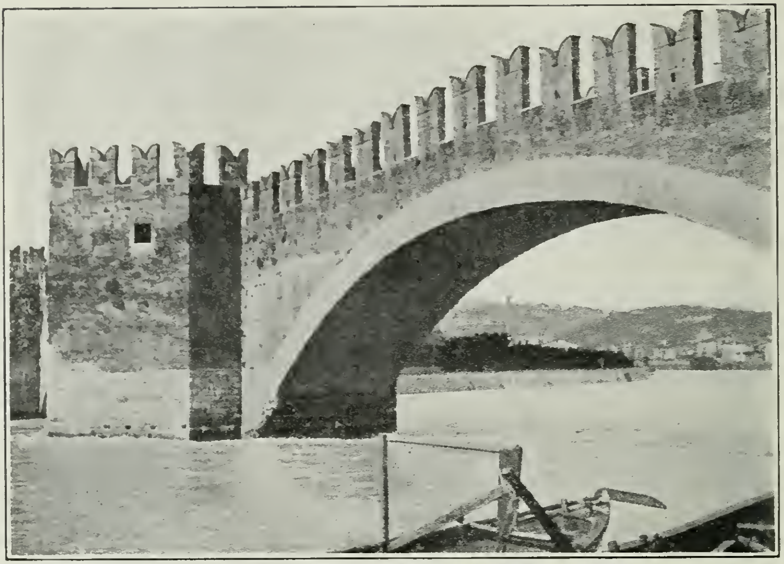
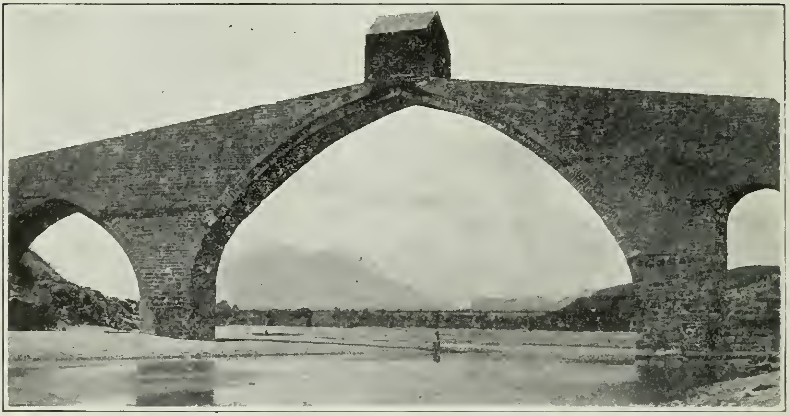
[2] Figs. 24, 25 and 26 have been taken from Paul Sejourné's "Grandes Voutes."

FIG. 26.



Castelvecchio Bridge, Verona.

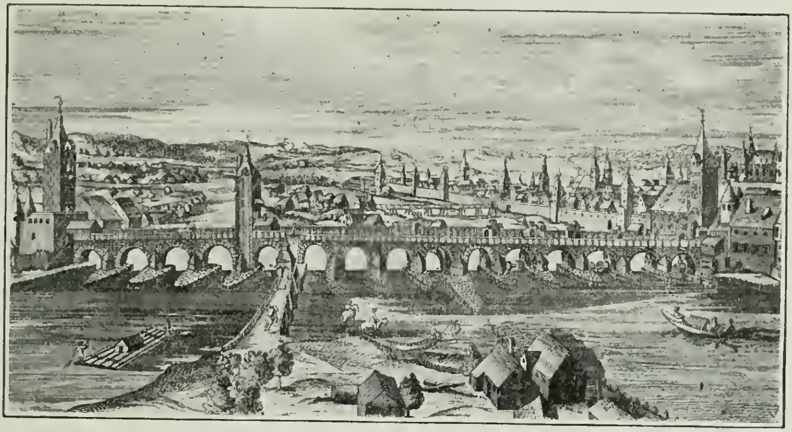
FIG. 27.



Devil's Bridge at Martorell.

and the top of the large arch, which has an opening of 145 feet, is held down by a chappel. The large arch has two superposed arch-rings and a third one near the upper part of the arch, which diverges from the other two at a point about one-third down from the summit and loses itself in the spandril walls. This method of superposed arch-rings without any interlocking between them is very characteristic of arches of the Middle Ages (Fig. 27).

FIG. 28.

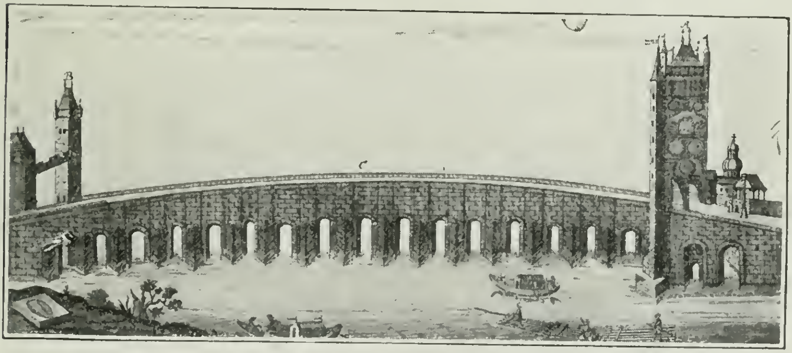


Regensburg Bridge, Austria.

LARGE STONE-ARCH BRIDGES OF THE XVIITH AND XVIIITH CENTURY.

Of the later bridges, one built in Regensburg, Austria, shows how little confidence the engineers had in the foundations, for they protected the piers by large cribs filled with stone, which cut off the greater portion of the waterway (Fig. 28).

FIG. 29.



Bridge at Prag.

The bridge at Prag was begun in 1638 but not finished until the beginning of the eighteenth century. At the time it was built it was one of the four largest bridges in existence. Also it was considered the widest one; its width between parapets being over 35 feet (Figs. 29 and 30).[3]

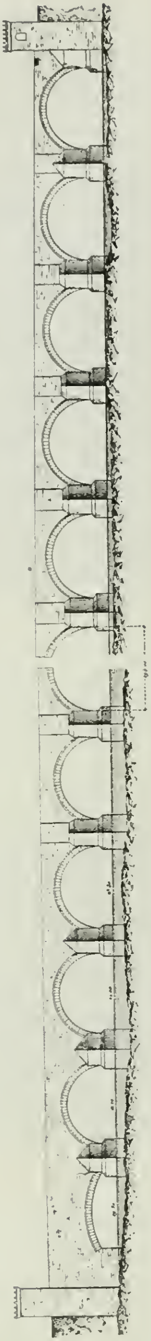


FIG. 30.

Bridge at Prag.

LONG-SPAN WOODEN BRIDGES OF THE XVIIITH CENTURY.

About one hundred years after the Prag bridge was built wood made a sudden reappearance as bridge material, this time for spans of considerable length. Two village carpenters, Jean and Ulrich Grubenmann, born at Teufen, Switzerland, began to build long-span bridges of timber, employing a most ingenious system of their own invention. In 1755 Ulrich began his bridge over the Rhine in Schaffhausen and completed it three years later. It consisted of two spans of a total length of 364 feet with a width of roadway of 18 feet. It was supported on masonry piers (Fig. 31). The bridge was covered with a roof—a practice generally and properly followed in most timber highway bridges of those times. At the same time Jean built a similar bridge at Reichenau with a span of 240 feet and a little later both brothers built the Wittingen Bridge near Baden with a single span of three hundred and ninety feet (Fig. 32). The length of this span is given by some authorities as only 366 feet. Even then it was an astounding achievement considering that calculations of stresses or even the strength of timber in compression were entirely unknown. Since the Grubenmann brothers, wooden bridge-building has made no progress in Europe. It was further developed in the United States but, as will be seen later, on entirely different lines.

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[3] Fig. 30 is added to correct the impression which Fig. 29 may give that the bridge was built on a vertical curve. While the picture is not as elaborate, it is probably more accurate.

SUSPENSION BRIDGES.

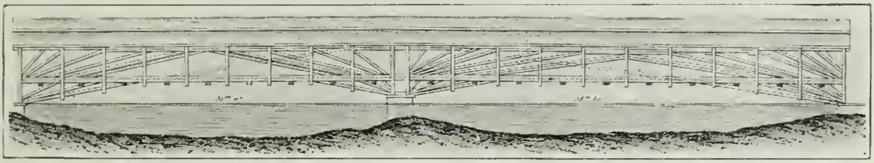
The suspension bridge is probably as old as other types and may have been originally inspired by vines hanging over a stream. There is a suspension foot-bridge in Guatemala near Lake Izabal which vividly suggests this origin (Fig. 33).

A cane bridge in Sikkim Valley, India, is another example of this simple and primitive construction (Fig. 34).

The first suspension bridge cables were either of wires or ropes and the floor followed closely the curve of suspension.

Leopold speaks of a very old suspension bridge in China built from rock to rock, consisting of twenty very heavy iron chains covered with planks. Here the rocks acted both as towers and as anchorages (Fig. 35).

Fig. 31.



Bridge at Schaffhausen, Switzerland.

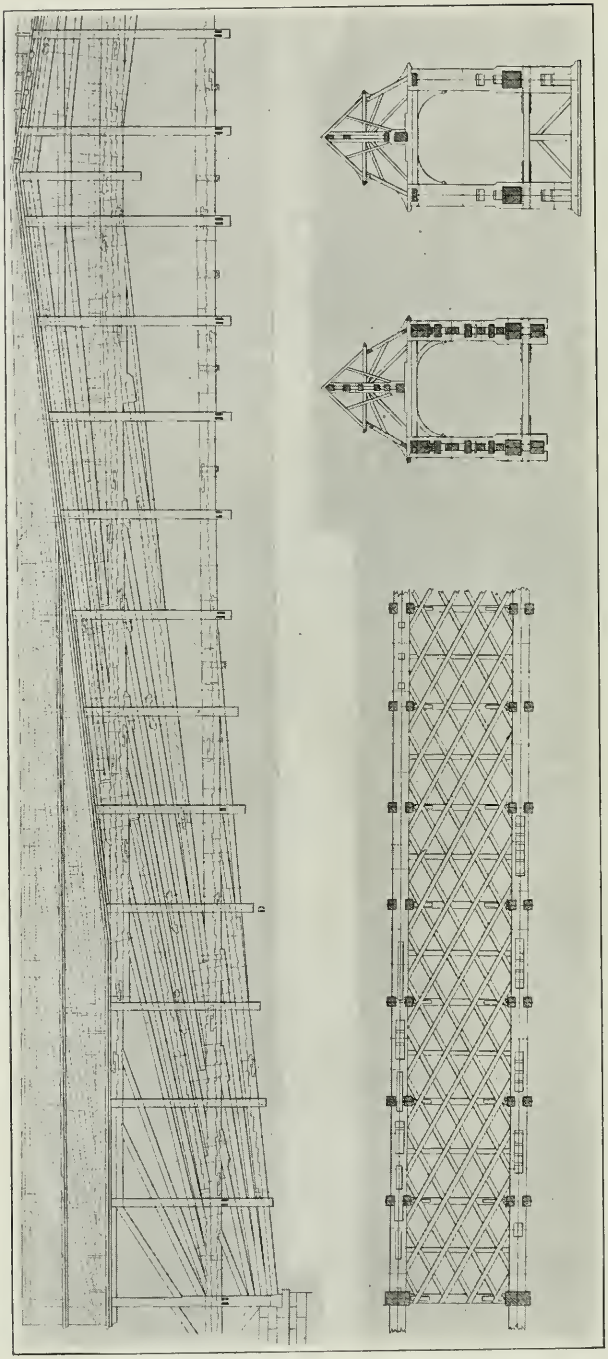
Not until the end of the eighteenth century was the idea carried out of suspending a horizontal roadway from the cables, although a very rare and ancient work, entitled "Machinæ novæ Fausti Verantii Siceni," illustrates the principle of the Faustus Verantius Bridge, calling it "portable and convenient for the armies" (Fig. 36).

In England in 1819 Sir Samuel Brown built a suspension bridge over the Tweed which had a span of 449 feet. In 1826 Telford completed his famous suspension bridge over the Menai Straits. It is still in very good condition. The span is about 580 feet and is hung from iron chain cables (Fig. 37).

The Americans seem to have preceded the Englishmen in building suspension bridges with chain cables of long spans. In 1808 there were over forty suspension bridges in the United States constructed under the Finley system. Engineer James Finley employed cables made of long chain links, and later, of iron bars.

The first wire-cable suspension bridge seems to have been one built over the Schuylkill River in 1815. It was a foot-bridge only,

FIG. 32.



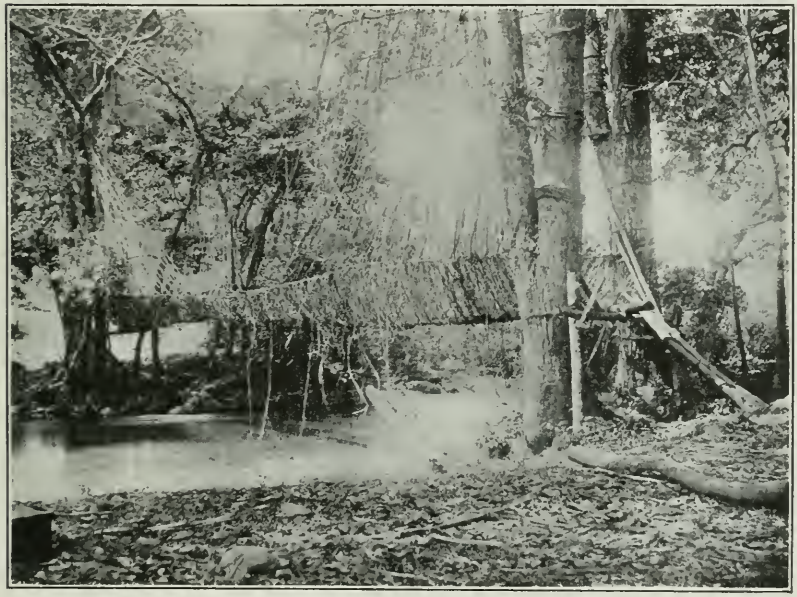
Bridge at Wittingen.

of 400 feet span. Since then the building of suspension bridges has made great progress and now they are recognized as the best-known form of construction for very long spans. Everyone is familiar with the New York bridges which are the longest suspension spans in the world.

DEVELOPMENT OF METAL BRIDGES.

Iron was known in China, India, and Egypt for a long time. Steel also was known about 500 B.C. but was not made in Europe until the thirteenth century. Cast iron, strange to say, came still later, but was the first to be used in metal bridges. Abraham Darby is credited with having built the first cast-iron bridge. In 1779 he completed the well-known bridge at Coobrookdale, England. It is an arch of 50 feet rise and 100 feet opening. This was followed by other cast-iron bridges in England as well as in France.

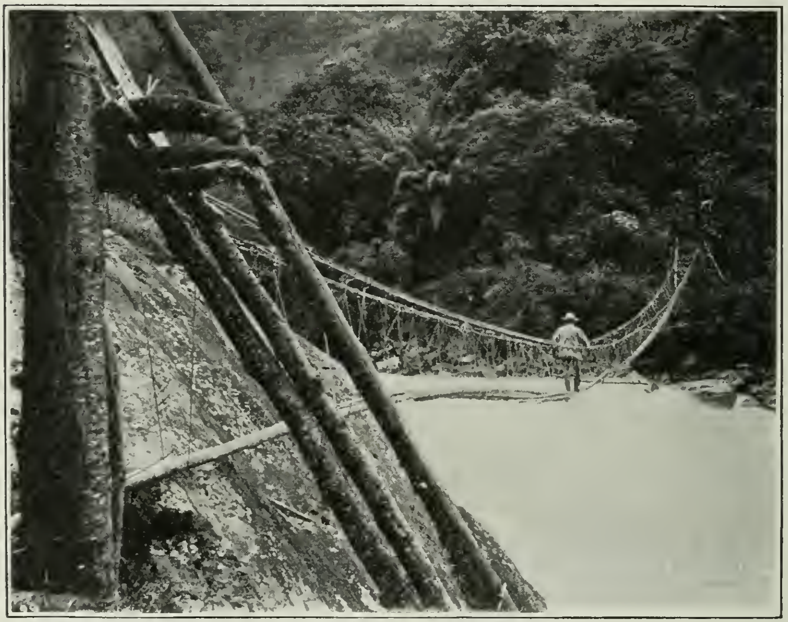
FIG. 33.



Foot-bridge near Lake Izabal, Guatemala.

In 1844 wrought iron was first used in bridge work in the form of girders. In 1850 Stephenson built the tubular bridge over Menai Straits. This was followed rapidly by other tubular bridges in England and Canada, some of their designs being more original than efficient. Most of them have stood well, however, probably because of large excess of material used. One of the most remarkable examples is the Saltash Bridge built by Brunel in 1858. It is a large, single, curved tube placed above the roadway and connected with curved bottom chords. The tube was made of elliptical section and its width was determined by the width of the roadway below. The two main spans are each 456 feet long. The bridge is said to be still in use (Fig. 38).

FIG. 34.



Foot-bridge in Sikkim Valley, India.

Experiments with tubular designs were soon followed by lattice girders and steel arches. In France lattice girders continuous over three or more supports were at first quite popular. Later, simple spans with curved top chord seemed to find more favor. A very neat design is that of a bridge near Dinan, France (Fig. 39).

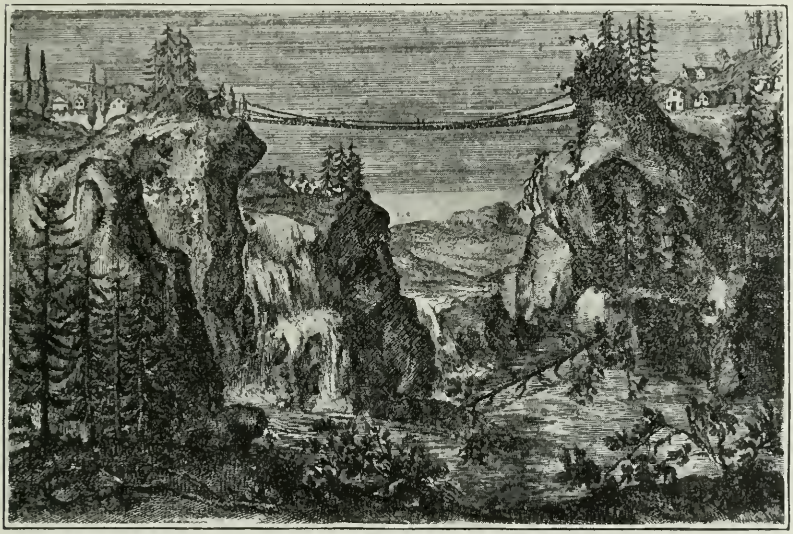
Probably the most decorative designs in steel were obtained by using arches. A beautiful example of such construction is seen in the Eads Bridge at St. Louis; another good example is the bridge at Coblenz, Germany (Fig. 40).

THE FORTH BRIDGE AND THE QUEBEC BRIDGE.

Then came the gigantic work of the Forth Bridge with 1790 feet spans (Fig. 41) and, lately, that of the Quebec Bridge with an 1800-feet span.

These two bridges have the longest spans in existence and are both of the cantilever system. Yet the methods followed in their design and construction were radically different. The Forth Bridge has all its compression members of tubular construction and all connections between the different truss members are rigidly riveted. In the Quebec Bridge the compression members are built of parallel webs latticed while the main tension members are of eye-bars; pin connections have been used throughout the trusses instead of riveted joints. In the Forth Bridge plates were shipped from the mills to the bridge site where they were bent, punched or drilled and fitted into place plate by plate, and the number of workmen in the field is said to have reached, at a certain time, six thousand. The Quebec Bridge members were manufactured in shops specially constructed for this work, and shipped in large

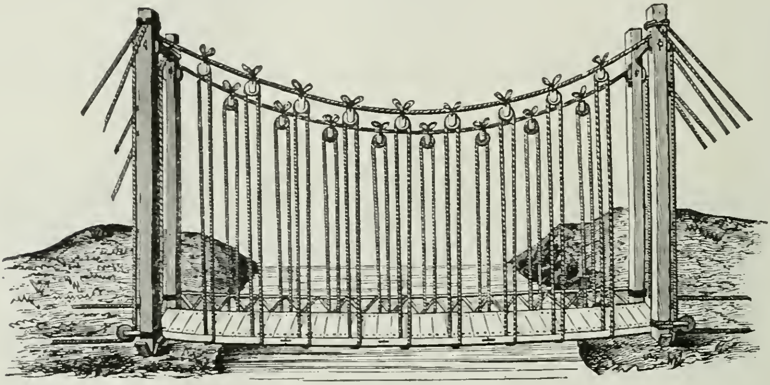
FIG. 35.



Suspension bridge in China.

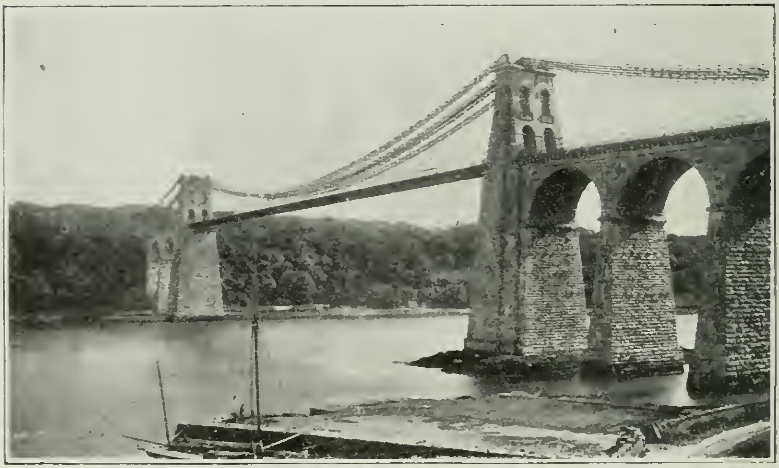
units to the bridge site, where driving of pins and some riveting was all that was necessary to assemble the structure. It is true that the Quebec work required much heavier lifting and handling machinery than the single plates of the Forth Bridge, but, on the other hand, the required amount of labor in the field was greatly reduced and a comparatively small force was used. In each instance, however, the particular method was justified. The Forth

FIG. 36.



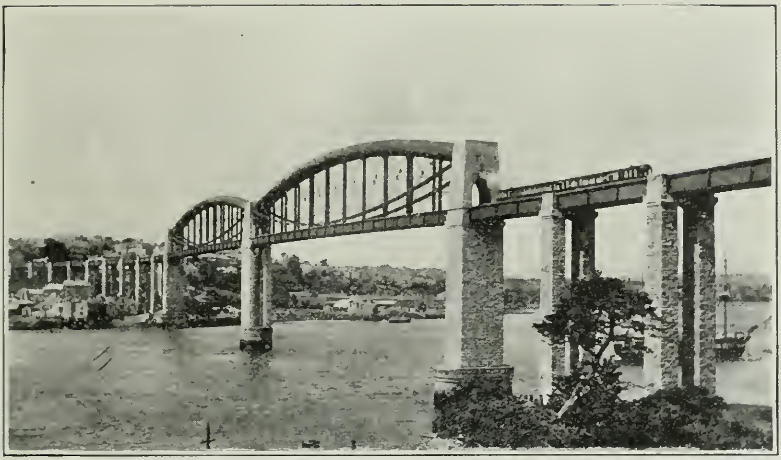
Pons Faustus Verantius.

FIG. 37.



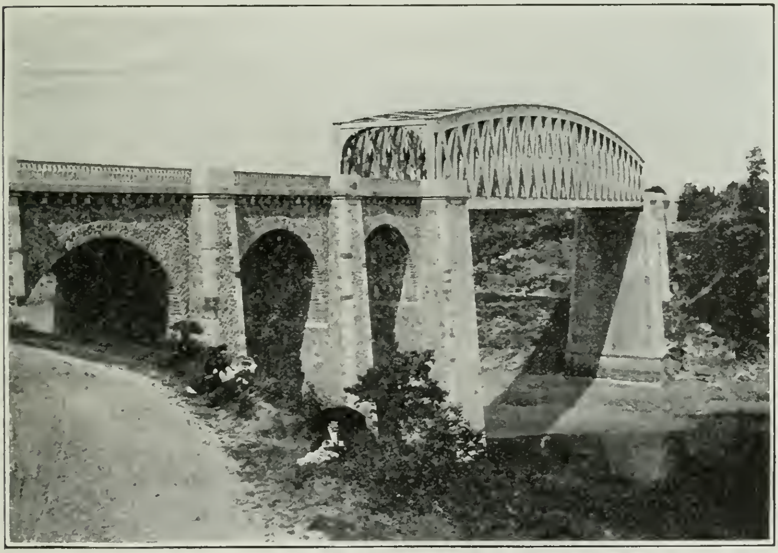
Bridge over the Menai Straits.

FIG. 38.



Saltash Bridge, Plymouth.

FIG. 39.



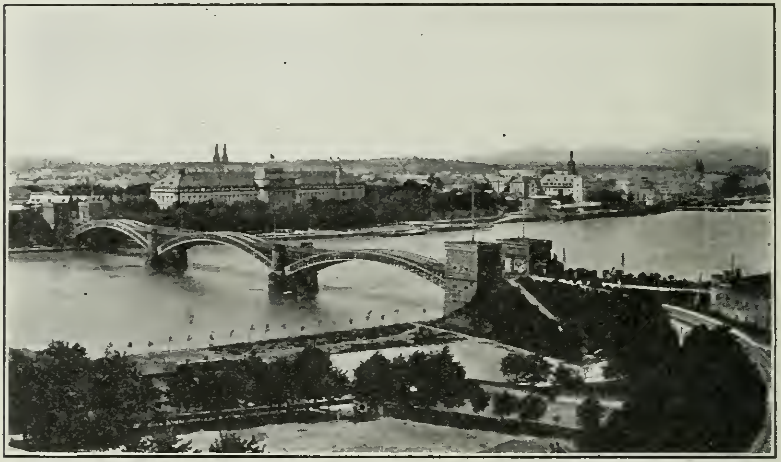
Bridge near Dinan, France.

Bridge method by the cheapness of labor at the time and place of its building and the Quebec Bridge method by the improved erection machinery and greatly increased cost of labor.

REINFORCED CONCRETE.

Within recent years a new heterogeneous material has come into wide use in engineering, not only for bridges but for other structures as well. Mehan and Monnier first demonstrated the value of steel reinforcement of concrete. There are now many examples of reinforced concrete bridges. As is usually the case with new things in construction, many failures have occurred; but the lessons from such failures together with theory, laboratory tests and the successful structures, go to make up the knowledge of correct design. This knowledge is not yet complete; one may say that it is in its infancy although it is growing rapidly; with a tendency to more caution and better judgment and less struggle for economy which is often only apparent and always dangerous.

FIG. 40.

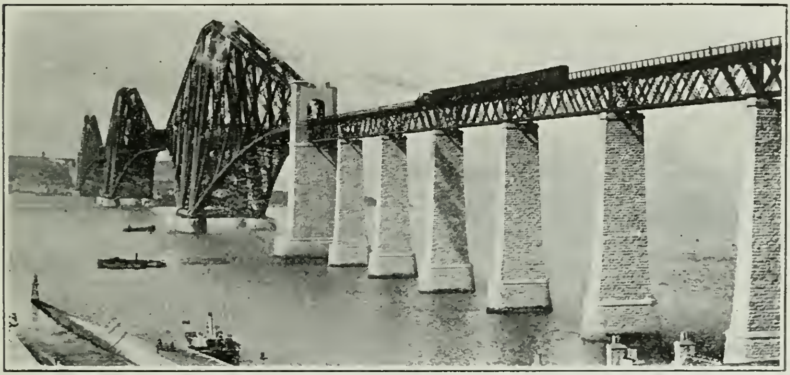


Arch bridge at Coblenz.

BRIDGE CONSTRUCTION IN THE UNITED STATES.

We have seen that wood was used in Europe as bridge material in the very beginning of civilization. In the United States, wood was again largely resorted to at first, in the early rapid development of its means of transportation. This, however, was due entirely to economic considerations, both from the point of expense and of celerity. During the very rapid development of the railroads in this country, it became necessary at first to use the cheapest and quickest means of bridging. The wooden truss was therefore used extensively during the first growth of the railroads and highways, to be replaced later by a more substantial and permanent form of construction. Among the early wooden structures, we are told of a quite remarkable one built by Louis Wernwag in 1813. It was a bridge over the Schuylkill River which had a span of 340 feet, supposedly the longest wooden bridge ever built in the United States. After several systems of wooden construction had been tried, with more or less success, the wooden Howe truss, invented by William Howe, made its appearance. The first structure of this type was built in 1840. It was a highway bridge with a 75-foot span. Due to its simplicity, facility and quickness of construction, the system soon became generally used by nearly all the railroads in this country. Even to this date those wooden truss bridges may be seen on some less prosperous railroad lines.

FIG. 41.



Firth of Forth, Scotland.

With the expanding iron industries, wrought and cast iron soon replaced wood, but the necessity still existed for quick and easy erection of bridges in the field, with the least amount of labor and machinery, and therefore engineers were exerting their ingenuity to invent systems of trussing which would meet those requirements. And so there came a period of the various systems, such as Bollman, Fink, Post, Linville, Pettit, Warren, Pratt, etc., most of which are now obsolete.

These systems were all based on connecting the truss members by pins, which greatly reduced the work of assembling in the field.

The pin-connected system is characteristic of American bridges and marked a great advance in this branch of engineering. It is now being replaced in smaller spans by riveted connections but in long truss spans, it is still the most practical method of construction.

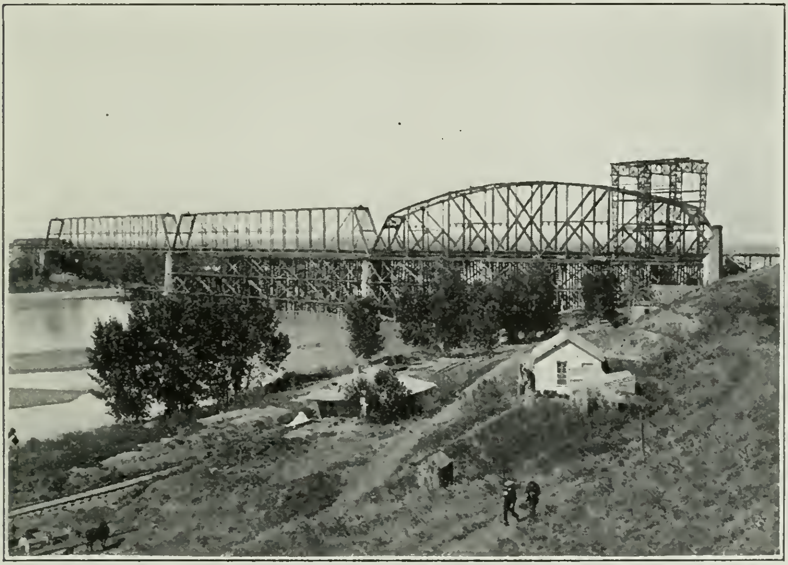
In these early times of bridge construction in this country, or prior to 1880, the metals used were wrought and cast iron exclusively; the only exception being the Eads Bridge in St. Louis, in which Captain Eads used chrome steel for the first time; and excepting steel used in the wires of suspension bridges, some of which were built prior to that year. In the meantime, iron mills began to manufacture steel, first Bessemer, then open hearth, and gradually cast iron was replaced by wrought iron which, in turn, was replaced by Bessemer steel and finally by the open-hearth steel which is now generally used.

In recent years alloys of steel have been used more and more —nickel steel, chrome-nickel steel and silicon steel. These materials, because of their increased strength, prove economical for long spans. For the same reason, they also make it possible to build longer spans than could practically be done with ordinary steel. We have not yet reached the full possibilities of alloys as bridge materials, and we may expect still greater progress in this direction.

Since the introduction of the metal truss, the form of trussing has undergone very marked changes due not only to progress in manufacture and in facilities for work in the field, but also to wider experience and the better understanding of theory. And so, as has been said before, many of the early ingenious systems bearing the names of their inventors were gradually abandoned until now only two of them are used, the Warren and the Pratt systems; the so-called sub-divided Pratt system, usually being given preference for long spans. The earlier through-bridges had trusses generally with parallel chords; later, trusses with parabolic top chords for independent spans, when the spans were of sufficient length, came into almost exclusive use. The Bismarck Bridge in North Dakota is one of the many examples of this change. Three four-hundred-foot spans, built in 1883 with trusses of double intersection Howe system with parallel chords, were replaced in 1905 by spans of the same length having trusses of the sub-divided Howe system and parabolic top chords (Fig. 42).

The United States, because of the rapid growth of its railways and the magnitude of its streams, offers the greatest opportunity of any country for the development of the science and knowledge of bridge-building. Unfortunately, we have now entered upon an era of standard specifications and each engineering society of any size is bent upon compiling its own. So that an engineer desiring to secure somewhat better material for his structure is met by objections from the manufacturer who claims that if the standard specifications of such and such society are good enough the engineer should be content with them. This automatically arrests any effort on the part of the contractor to produce better material than what is known by him as "commercial product" and thus progress in the manufacture of materials of higher grade quality for bridge work is retarded. The material is not improving in quality—it is even deteriorating. Standard specifications are an advantage in many cases, but not in regulating the product of industries which are still almost in their infancy and in process of development.

FIG. 42.



Bismarck Bridge, North Dakota.

But the modern-bridge engineer is far from having the privileges of Pontifex Maximus. Leupold quotes the following interesting description of those privileges:

"What great consideration the bridges and their conservation occupied with the ancients and especially with the Romans is sufficiently illustrated by the following:

"That the office of building and conserving such (bridge) should be given and entrusted to a person bearing the title of a Pontifex Maximus, which person was *exempt* above all other persons and even possessed the highest direction of the then pagan service of God, and who completely possessed all power in religious matters to do and to let as he found fit. Yea, the position was so great and important that a great emperor, Augustus, and after him many other pagan and Christian emperors, attached this title to their imperial dignity. And while the Christian emperors did not apply such office in a pagan way, they utilized it as Christians to represent by it the highest person in the spiritual as well as in the wordly society. For, a Pontifex Maximus was bound by no law and did not have to give account of his doings to the people nor to the Council; could not be called for penalty; no one dared attack him by word; kept such dignity and office during his lifetime; no one equal to him was appointed; could let himself be carried into the Capitolium, which was not permitted to any other man and besides was an asylum for persecuted criminals."

And if we wish to know what requirements one had to possess to be a bridge engineer two hundred years ago, one should read in Leupold's work the following:

"Since bridge-building is to be considered as being among the foremost and most important works of man, in which all human understanding, wisdom, experience, in fact, all arts and sciences, must coöperate, such an 'Architecto' must not only be experienced in arithmetic and geometry, so as to be able to measure precisely the length, breadth and depth of a stream, to plat all this correctly and accurately on a geometrical plan, to estimate quantities of all materials, as stone, timber, lime, iron work, and finally, to determine the cost of construction; but he must also be a good physicist, to well understand all properties of the materials of construction and distinguish between their faults and merits, particularly, which wood is best, when it should be cut and to what purpose each kind serves; also the properties of the water, of the ice, how and where it exerts its greatest force and how such a force can best be overcome; he must above all have a good understanding of the ground and bottom of the river in which the piles or piers are to stand; he must also have a sufficient knowledge of mechanics, partly to indicate or apply machinery for procuring, lifting and lowering the large beams, piles, stones, etc., and for driving piles by means of convenient hammers; partly to be able to indicate various methods for lifting the water out of cofferdams, or to drive the cofferdams themselves, and to lift the water from around the piers or where it is desired to reach the ground; and, above all, he must be a good carpenter and stone mason, both being equally the foremost and principal part in the building of a bridge; because if the bridge is entirely of wood, then it falls entirely to the carpenter; if, however, it is of stone, then has the carpenter one of the most important works to perform in building scaffolding and centres, and the stone mason must not let his art be without experience either; and the knowledge of the law of gravity is here mainly required so one would know how the bodies press and where the greatest effort comes and where those forces can best be resisted; to sum up, there are so many things required that space is here too small to touch upon all of them."

REFERENCES.

JEAN RONDELET: "L'Art de Bâtir," Paris, 1832.
JACOB LEUPOLD: "Theatrum Pontificiale," Leipzig, 1726.
BERNARD DE MONFAUCON: "L'Antiquitée Expliquée," Paris, 1722.
EMILAND GAUTHEY: "Traité de la Construction des Ponts."
MORANDIÈRE: "Traité des Ponts."
PAUL SEJOURNÉ: "Grandes Voutes."
CHOIZY: "L'Art de Construire chez les Romains."
E. PONTZEN: "Les Chemins der Fer en Amérique."
FRANK BRANGWYN and W. SHAW SPARROW: "Book of Bridges."
CLÉMENT PELLE: "L'Empire Chinois," illustrated by Thomas Allom.

Samuel Latham Mitchill—a Father in American Chemistry.—The Chandler Medal for 1922 has been awarded to Edgar Fahs Smith by Columbia University. At the conferring of the medal, Doctor Smith delivered an address on "Samuel Latham Mitchill—a Father in American Chemistry" (*Jour. Ind. Eng. Chem.*, 1922, xiv, 556–560). Mitchill was a native of Long Island, was educated in medicine at Edinboro, and became professor of chemistry in Columbia in 1792 at the age of 28 years. He was an ardent antiphlogistonist and a pioneer in the study of the application of chemistry to the arts and to sanitation. He also made contributions to geology, mineralogy, and ichthyology, assisted in the preparation of the United States Pharmacopœia, and founded *The Medical Repository* which became a journal of general science and contains many of the earliest American contributions to chemistry. In addition to his scientific and educational work, Mitchill served as a member of the New York legislature and represented that state in the United States House of Representatives and Senate. J. S. H.

Rapid Electrolysis without Rotating Electrodes.—GRAHAM EDGAR and R. B. PURDUM, of the University of Virginia (*Jour. Am. Chem. Soc.*, 1922, xliv, 1267–1270), have devised a method for the rapid determination of metals by electrolysis with stationary electrodes. By use of a simple glass apparatus, the solution is stirred indirectly by a current of air during the electrolysis. A 110-volt lighting circuit, reduced by resistance lamps, was used as a source of current. As much as 4 decigrams of metallic copper were deposited quantitatively in 20 minutes. The method was used for the quantitative determination of silver, lead, copper, cadmium, iron, zinc, cobalt, and nickel. J. S. H.

Colorimetric Determination of Hydrogen Peroxide.—M. L. ISAACS, of the University of Cincinnati (*Jour. Am. Chem. Soc.*, 1922, xliv, 1662–1663), describes the following reaction of hydrogen peroxide. Thirty c.c. of water, 10 c.c. of 5 per cent. solution of citric acid, and 1 c.c. of dilute solution of hydrogen peroxide are mixed; and 1 c.c. of 10 per cent. solution of ammonium molybdate is slowly added. A yellow color develops. This reaction may be used for the colorimetric determination of hydrogen peroxide. The yellow solution is diluted to a volume of 50 c.c., and is compared in a Duboscq colorimeter with a standard solution of potassium chromate. This solution contains 0.4 gram of potassium chromate per litre, and is standardized against the color yielded by hydrogen peroxide of known concentration. J. S. H.

Functions of Aluminium in Living Matter.—JULIUS STOKLASA (*Umschau*, 1922, xxvi, 134–135) has studied the functions of aluminium in living matter. Thus aluminium protects plants from the injurious action of an excess of iron. By virtue of this property, aluminium promoted the growth of plant life during the carboniferous period, and thus made possible the coal deposits. In conjunction with iron and manganese, aluminium plays a part in the formation of the pigments in the blossoms of plants. The blue, violet, red, and blue-green pigments in birds and beetles owe their origin in part to the action of aluminium. This element is also present in the blood. J. S. H.

THE STABILITY OF ATOM NUCLEI, THE SEPARATION OF ISOTOPES, AND THE WHOLE NUMBER RULE.*

BY

WILLIAM D. HARKINS, Ph.D.
Department of Chemistry, University of Chicago.

26. THE NUCLEUS CONSIDERED AS A PROTON-ELECTRON AGGREGATE.

Up to this point the nucleus of a complex atom has been considered to be built up largely from alpha particles, and for this point of view considerable evidence has been presented. However, it will be of advantage from the standpoint of simplicity to study some of the relations which emerge when the nucleus is considered simply as a proton-electron aggregate, without reference to any groups into which they may be gathered inside the nucleus.

If only the lighter elements up to atomic number 16 are considered, it is found that while the number of protons in the atom is equal to the number of electrons, all of the protons, but only half of the electrons, are present in the nucleus, while the remaining half of the electrons form the planetary system outside. Thus the magnesium atom consists of 24 electrons and 24 protons, with all of the protons, but only 12 electrons in the nucleus. Strictly speaking, this relation is exactly true only in the case of the most abundant isotope of an even-numbered element. In the case of the odd-numbered elements, the number of electrons in the atom is an odd number which is not divisible by two, and the number of electrons in the nucleus is equal to the whole number next larger than half the total number. Thus the aluminium atom consists of 27 protons and 14 electrons in the nucleus together with 13 planetary electrons. This last number is equal to 27 minus 14, or 13, which is the net positive charge on the nucleus. Fig. 4 illustrates these numerical relations in a number of typical cases.

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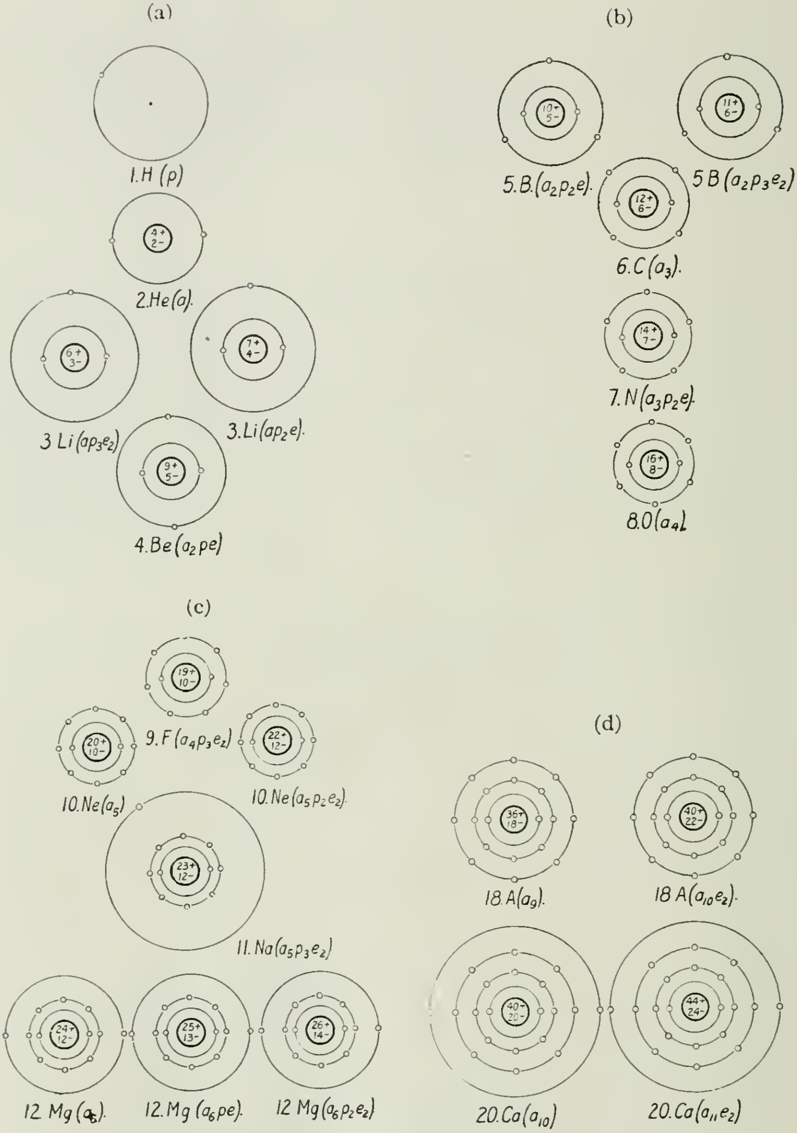
* Continued from page 211, vol. 194, August, 1922.

FIG. 4.



Diagrammatic representation of the composition of atoms. Each small open circle represents a planetary electron, and the figures inside the heavy circles give the number of protons (+) and of electrons (−) in the nucleus. The isotopes of lithium (Li), boron (B), neon (Ne), magnesium (Mg), argon (A), and calcium (Ca) are given. The second isotope of argon and the first of calcium are isomeric, since both have the composition $+_{40}$ $-_{40}$, and the nuclei of their atoms are practically isobaric (at. wt. = 40). While the planetary electrons are given in a plane, they may be supposed to be arranged in a three-dimensional space.

27. STABILITY CONDITIONS AND RELATIONS FOR ATOM NUCLEI.

Astronomers have had great difficulty in the exact treatment of the three-body problem, and it is readily seen that all known complex nuclei contain, according to our present theories, more than this number of particles. If the uranium nucleus is supposed to be made up of protons and electrons, there are 238 of the former and 146 of the latter, or 384 in all. Even if only the alpha particles assumed to be present are considered, it is evident that there are 59 particles at least to be taken into account. The problem of nuclear stability is therefore one in which the number of bodies is very large, so no exact mathematical treatment of the subject is possible. However, the writer has pointed out the most general relations which must be fulfilled in order that an atom may be stable. These general relations were found by the application of a general principle whose applicability was pointed out in 1916.[29]

This general principle may be stated as follows:

The relative abundance of the different atomic species in known materials—including the material of the meteorites, the surface of the earth, and what is known of the composition of the stars and nebulæ—*gives an index which points out the most important of the stability relations of the different types of atoms.* In addition to the data on the relative abundance of different atomic species, we have for the heaviest or radioactive atoms, data concerning their actual stability with respect to disintegration. It should be kept in mind, too, that there are different types of stability; thus a nucleus may be very stable with respect to an alpha disintegration, and quite unstable with reference to a beta disintegration, and *vice versa.* Also there may be instability with reference to the emission of protons, possibly with a concomitant emission of electrons, as in the disintegration experiments of Sir Ernest Rutherford.

The most general of all of the stability conditions may be expressed as follows:

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[29] HARKINS: *J. Am. Chem. Soc.*, **39**, 856-877 (1917); *Proc. Nat. Acad. Sciences*, **1**, 186-214 (1916).

In JOURNAL OF THE FRANKLIN INSTITUTE, **193**, pp. 603, 604, and pp. 109 and 110 of a book on Isotopes, the relations listed here have been published without any reference to their earlier publication by the present writer.

1. *No atom has been discovered in which there is less than one electron to each two protons*, so it may be concluded that the most general stability condition is: *No nucleus is stable unless the number of electrons it contains is equal to or greater than half the number of protons.* It is of extreme interest that in most atomic species which are found in meteorites and in the earth's crust, the number of nuclear electrons is exactly equal to half the number of protons. Furthermore, in the alpha particle, from which all atom nuclei are almost entirely built, the numerical relations are also exactly these simple ones.

The second stability relation is given as follows:

2. *As the nucleus becomes more positive with reference to its net content of positive electricity, it is essential for stability that it shall become more negative with reference to its relative content of negative electrons.*

In addition to the above three relations of primary importance, there are others which are less general, and these will be outlined later.

This principle indicates that for each element there is only a limited range of relative negativeness in which atoms can have enough stability to exist, which means that the number of stable isotopes is not very large, and is limited to certain range of atomic weights, or of isotopic numbers.

The third stability principle relates to the negative electron content of the nucleus:

3. *The number of negative electrons in most atom nuclei is even.* Thus there are about 40 times as many atoms in the earth's crust which contain an even number of nuclear electrons, as there are of those in which this number is odd. In the meteorites the ratio is 33 to 1.

Thus, *nuclei, or groups of electrons and protons in nuclei, which contain an odd number of negative electrons, are in general much less stable than those which contain an even number.*

While the abundance relation stated above refers to the occurrence of individual atoms, it is apparent that the stability principle deduced from it should have an application concerning the number of the various types of atomic species in existence. *Thus there should be many more atomic species* (isotopes) *with an even than with an odd number of nuclear electrons.* This principle has received an ample verification since its first announcement.

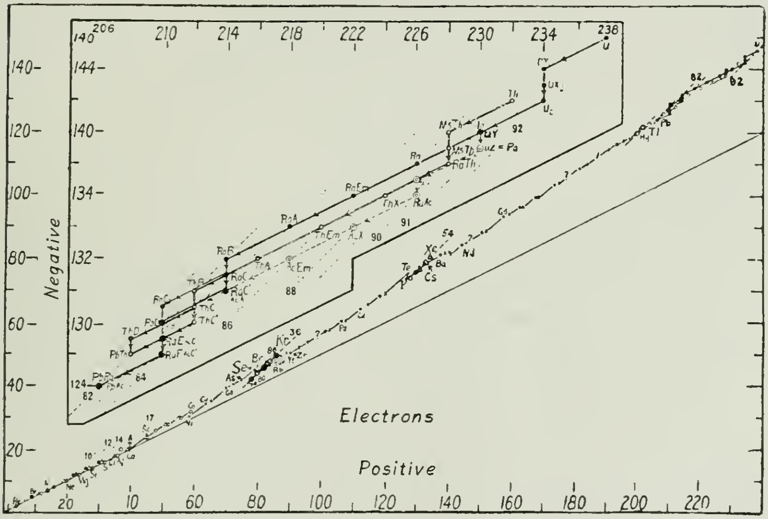
NOTATION.

P atomic weight, or number of positive electrons.
M atomic number, or positive charge on nucleus.
N $P-M$, or number of negative electrons in the nucleus.
n isotopic number.
p a positive electron.
e a negative electron.
a an alpha particle.
pe a neutron.

Using the above notation, the first general stability relation discussed above may be expressed in a general form as follows:[30]

In complex nuclei the number of electrons is never less than half the number of protons, or the ratio N/P is never less than one-half. Thus the number of protons is never larger than twice the number of electrons, or P/N is never greater than 2.

FIG. 5.



Since $P - N = M$ it is evident that *the number of positive electrons in an atom* (or the atomic weight) *is always equal to or greater than twice the net positive charge on the nucleus* (atomic number), so $P/M = 2$, or $M/P = \frac{1}{2}$.

The relation between the number of positive and negative electrons in atom nuclei is shown in Fig. 5. It may be seen that while the light atoms lie very nearly on a line of a slope equal to ½, the number of negative electrons steadily increases above the value given by this line as the nucleus becomes heavier. The radioactive elements are plotted in the upper part of the diagram, which shows that during a series of alpha changes the elements remain upon a line with a slope of ½, or exactly that for the light atoms.

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[30] Harkins: *J. Am. Chem. Soc.*, 42, 1965–85 (1920).

The number of negative electrons in light nuclei is equal to (or only slightly greater than) the atomic number (Fig. 7), while the number of positive electrons is twice the atomic number (Fig. 6). The two figures (6 and 7) exhibit the important relation that

Fig. 6.

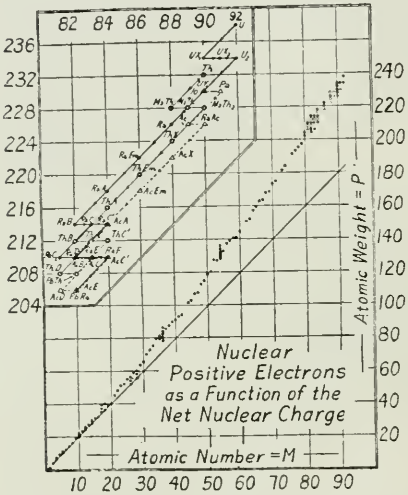
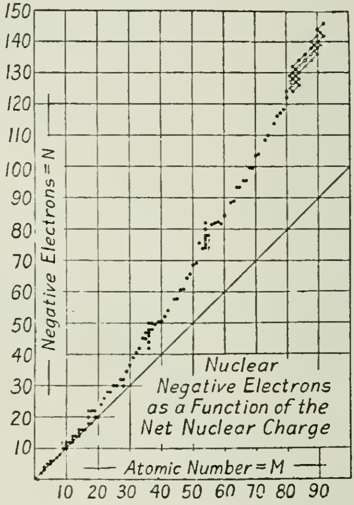


Fig. 7.



the number of electrons in any nucleus, in excess of the number represented by the inclined straight line, is the same in both figures (6 and 7), so in either figure the height of any point above the inclined line, represents the number of neutrons (pe) in the nucleus in excess of the composition represented by the formula $(p_2e)_M$. The number of neutrons found in this way will be designated later as the isotopic number of the atomic species.

28. THE ISOTOPIC NUMBER.

It is evident that so long as only one atomic species was known to exist for each of the 92 elements, that a single number for each element, the atomic number, was sufficient to designate all of the atomic species known. However, as soon as it was found that each element may consist of several atomic species, or isotopes, it became evident that a second number was necessary. While the number usually chosen for this purpose has been the atomic weight, it is evident that there is another number which is more suited as a basis for the classification of isotopes. This number has been designated by the writer as the *isotopic number.** The isotopic number may be defined as the number of neutrons (pe) in a nucleus in excess of the composition represented by the formula $(p_2e)_M$. It was first made evident in the following way: If the number of positive electrons in the nucleus is represented on the X-axis, and the relative negativeness minus 0.5, or $(\frac{N}{P} - 0.5)$, is plotted on the X-axis, it is found that all atomic species lie either on the X-axis (isotopic number 0) or upon one of 54 equilateral hyperbolas (isotopic numbers 1 to 54), as is shown in Fig. 8. These hyperbolas are represented by the equation $P(\frac{N}{P} - 0.5) = 0.5\ n$, or $n = 2P\left(\frac{N}{P} - 0.5\right)$, so

$$n = P - 2M \qquad (1)$$

$$n = 2N - P \qquad (2)$$

$$n = N - M \qquad (3)$$

Equation 1, which may be written $P = 2M + n$ shows that *the isotopic number is that number which, when added to twice the atomic number, gives the atomic weight.* Equation 2 indicates that it is also the *excess of twice the number of nuclear negative electrons over the number of protons,* and equation 3, that it represents the *excess of the number of nuclear negative electrons over the net positive charge on the nucleus.*

The lower right-hand corner of Fig. 8 represents the radioactive elements. It is evident that *in an alpha disintegration the isotopic number remains constant, while a single beta disintegration decreases the isotopic number by two.* Of these two units one is due to the decrease of N by one, and the other to the concomitant *increase* of M by one.

The addition of a negative electron to any nucleus would increase its isotopic number by two, but decrease its atomic number by one, while the addition of a positive electron would decrease its isotopic number by one, and increase its atomic number by one. The three isotopes of magnesium may be designated as Mg 12_0^{24}, 12_1^{25}, and 12_2^{26}, with the isotopic number (n) written as a subscript. While the atomic weight is given as a superscript, it is superfluous, since its value is always twice the atomic number (12 in this case) plus the isotopic number. The addition of a positive electron to the nucleus of Mg 12_2^{26} would give 13_1^{27}, which is aluminium. The addition of a negative electron to the nucleus of Ca 20_0^{40} would give K 19_2^{40}, and of a second negative electron would give A 18_4^{40}, which is the most abundant isotope of argon. Thus the nuclei of the most abundant isotopes of calcium and argon, both with an atomic weight equal to 40, differ by 2 negative electrons, and in that the isotopic number of the former is 0, while that of the latter is 4.

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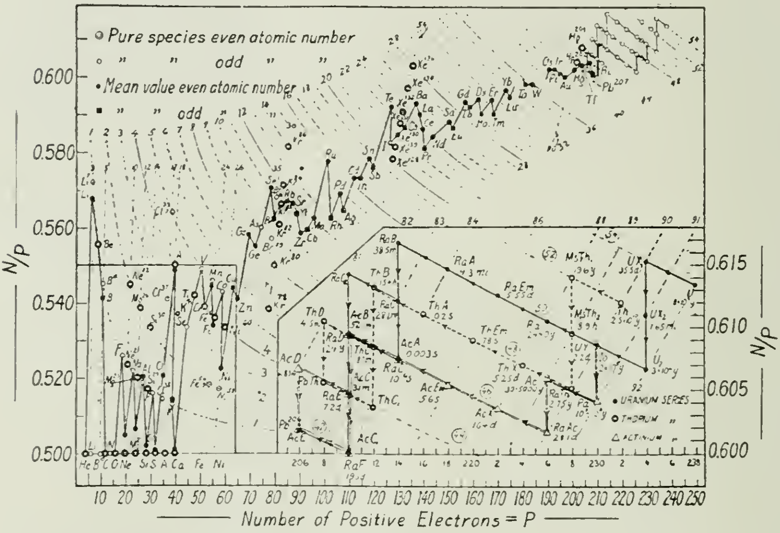
* When first used by the writer [*J. Am. Chem. Soc.*, **42**, 1971 (1920) and **37**, 1380, 1385, 1386, 1395 (1915)] the number was one-half that given in the later papers. It is evident that the half-values give the same system of classification, but involve the use of numbers which are not all integers. Masson [*Phil. Mag.*, 41, 281–5 (1921)] has used the present system of notation.

Fig. 8.

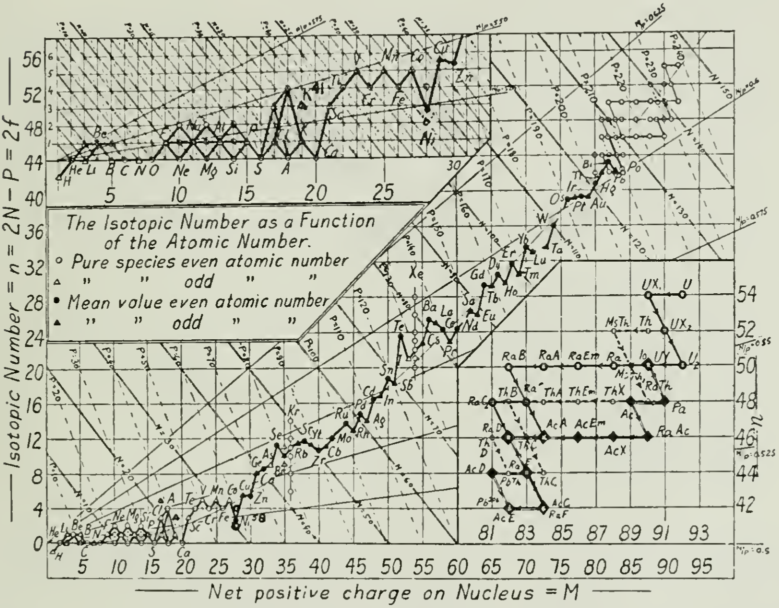


29. ISOTOPIC AND NEUTRONAL LINES.

A line upon which all of the isotopes of a single element lie in Fig. 8 or any other diagram, may be called an *isotopic line.* In the figure these are nearly vertical, but incline slightly to the right. A line upon which atomic species of a single isotopic number lie, may be called a *neutronal line,* since the number of such a line gives the number of neutrons in the nucleus in excess of the normal composition represented by the formula $(p_2e)_M$.

The neutronal lines may be considered as representing levels, which in a radioactive series are related to the number of beta particles emitted by the nucleus. It is of interest that in the thorium and uranium disintegration series, and also in the actinium series, as given by most workers on radioactivity, all of the neutronal lines, which represent paths of disintegration, have even numbers. The isotopic number of thorium is 52, which indicates that if thorium were to disintegrate completely into helium, the number of beta particles (cementing electrons) emitted would be 26, or in general the number of beta particles emitted in the complete disintegration into helium of any element whose isotopic number is divisible by 4, is one-half of the isotopic number.

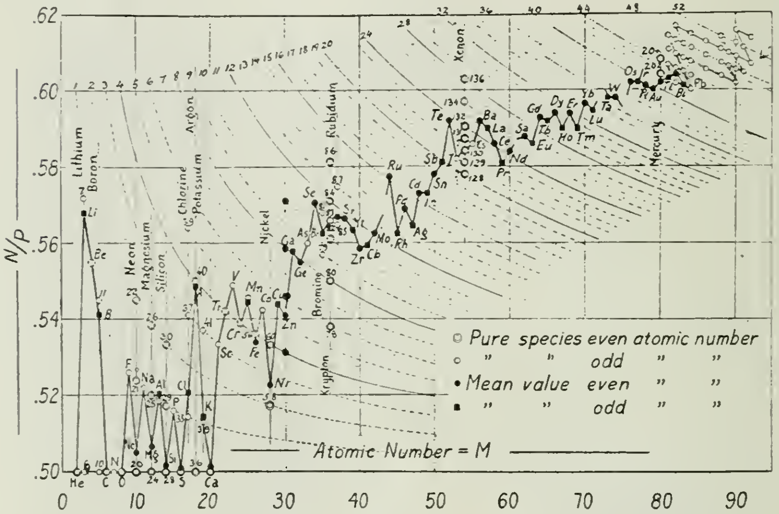
FIG. 9.



In Fig. 9 the isotopic lines are vertical, and the neutronal lines are horizontal. In this plot isobaric atoms, such as Ca_0^{40} and A_4^{40}, lie on lines whose slope is −2, and those with a constant number of nuclear negative electrons lie on a line whose slope is −1. The region of stability in which atoms exist has in this plot the general form of an hyperbola. The heavy lines in the radioactive portion of the plot represent disintegration series, but those in the other parts of the figure show merely the periodicity; mainly of the mean values.

Fig. 9 has the remarkable characteristic that it plots the values of five variables: *n, M, P, N,* and *N/P,* in a plane, and

FIG. 10.



that constant values for the first four of these variables are represented by straight lines which are parallel, and for the fifth by straight lines which radiate from the origin.

30. SECOND STABILITY PRINCIPLE: INCREASE OF THE RELATIVE NEGATIVENESS OF ATOM NUCLEI AS THE NET POSITIVENESS INCREASES.

The first stability principle states that the number of electrons in an atom nucleus is never less than half the number of protons, or the ratio *N/P* is always equal to, or greater than, ½. Now, the most abundant light atoms up to atomic number 20, are those in which this ratio has exactly the value 0.5, so it is of interest to inquire as to what values this ratio takes as the atomic number rises above the value 20. Fig. 10 shows the general variation of the ratio as the atomic number increases, and indicates that for

TABLE XVI A.

Values of the Relative Negativeness N/P of the Nuclei of Radioactive Atomic Species, together with the Isotopic Numbers.

Uranium Series in Order of Disintegration.

Element.	Net positive charge.	Atom.		Positive elec-trons.	Nega-tive elec-trons.	α-Par-ticles.	N/P	Electrons.		
								Ce-ment-ing.	Ex-cess.	For-mula.
U.......	92	U	54	238	146	59	0.614	26	28	27
Th......	90	UX_1	54	234	*144*	*58*	*0.616*	*26*	*28*	*27*
Bv......	91	UX_2	52	234	*143*	*58*	*0.612—*	*25*	*27*	*26*
U.......	92	U_2	50	234	142	58	0.607	24	26	25
Th......	90	Io	50	230	140	57	0.609	24	26	25
Ra......	88	Ra	50	226	138	56	0.611	24	26	25
Nt......	86	RaEm	50	222	136	55	0.613	24	26	25
Po.......	84	RaA	50	218	134	54	0.615	24	26	25
Pb......	82	RaB	50	214	*132*	*53*	*0.617*	*24*	*26*	*25*
Bi.......	83	RaC	48	214	*131*	*53*	*0.612*	*23*	*25*	*24*
Po......	84	RaC′	46	214	130	53	0.608	22	24	23
Pb......	82	RaD	46	210	*128*	*52*	*0.610*	*22*	*24*	*23*
Bi.......	83	RaE	44	210	*127*	*52*	*0.605*	*21*	*23*	*22*
Po......	84	RaF	42	210	126	52	0.600	20	22	21
Pb......	82	RaG	42	206	124	51	0.602	20	22	21

Secondary Branch of Uranium Series

Pb......	82	RaB	50	214	*132*	*53*	*0.617*	*24*	*26*	*25*
Bi.......	83	RaC	48	214	131	53	0.612	23	25	24
Tl.......	81	RaC_2	48	210	*129*	*52*	*0.614_3*	*23*	*25*	*24*
Pb......	82	End	46	210	128	52	0.609_5	22	24	23

TABLE XVI B.

Thorium Series in Order of Disintegration.

Th......	90	Th	52	232	142	58	0.612	26	26	26
Ra......	88	$MsTh_1$	52	228	*140*	*57*	*0.614*	*26*	*26*	*26*
Ac......	89	$MsTh_2$	50	228	*139*	*57*	*0.610*	*25*	*25*	*25*
Th......	90	RaTh	48	228	138	57	0.605	24	24	24
Ra......	88	ThX	48	224	136	56	0.607_1	24	24	24
Nt......	86	ThEm	48	220	134	55	0.609_1	24	24	24
Po.......	84	ThA	48	216	132	54	0.611_1	24	24	24
Pb......	82	ThB	48	212	*130*	*53*	*0.613_2*	*24*	*24*	*24*
Bi.......	83	ThC	46	212	*129*	*53*	*0.608_6*	*23*	*23*	*23*
Po......	84	ThC′	44	212	128	53	0.603_8	22	22	22
Pb.......	82	PbTh	44	208	126	52	0.606	22	22	22

Secondary Branch of Thorium Series

Pb......	82	ThB	48	212	*130*	*53*	*0.613_2*	*24*	*24*	*24*
Bi.......	83	ThC	46	212	129	53	0.608_6	23	23	23
Tl.......	81	ThD′	46	208	*127*	*52*	*0.610_5*	*23*	*23*	*23*
Pb......	82	End?	44	208	126	52	0.606—	22	22	22

atoms of moderate abundance the range in the values of N/P is much greater for light than for heavy atoms. Thus the two isotopes of lithium exhibit a difference of slightly more than seven-hundredths, while in the whole radioactive region the extreme range thus far found is less than one-third as great. Thus there is a broad stability band, narrowing toward the right, extending from the lower left to the upper right-hand corner of the figure.

For the purposes of the present discussion Fig. 10 should be a three-dimensional diagram, the third dimension being taken to represent the abundance of the atomic species. The details of this three-dimensional plot will be discussed later, but it is apparent that there is a general increase in the value of N/P as M increases. It is also apparent that for any single isotopic number the value of the ratio *decreases* as the atomic number increases, so the second stability principle indicates that there should be a rapid general increase in the isotopic number with the atomic number. Since the principal isotope of element 92 has an isotopic number 54, the mean increase is 0.6 of an isotopic number per atomic number.

TABLE XVI C.

Actinium Series (Assumed to be Derived from U^2).*

Element.	Net positive charge.	Atom.		Positive electrons.	Negative electrons.	α-Particles.	N/P	Electrons.		
								Cementing.	Excess.	Formula.
Th.......	90	UY	50	230	140	57	0.608_8	24	26	25
Pa.......	91	Pa	48	230	139	57	0.604_3	23	25	24
Ac.......	89	Ac	48	*226*	*137*	*56*	*0.606_2*	*23*	*25*	*24*
Th.......	90	RaAc	46	226	136	56	0.602—	22	24	23
Ra.......	88	AcX	46	222	134	55	0.603_6	22	24	23
Nt.......	86	AcEm	46	218	132	54	0.605_4	22	24	23
Po.......	84	AcA	46	214	130	53	0.607_5	22	24	23
Pb.......	82	AcB	46	*210*	*128*	*52*	*0.609_5*	*22*	*24*	*23*
Bi.......	83	AcC	44	210	127	52	0.605	21	23	22
Po.......	84	AcC′	42	210	126	52	0.600	20	22	21
PbAc....	82	AcE	42	206	124	51	0.602	20	22	21
Pb′.......	82	AcD	44	206	124	51	0.602	20	22	21

P = no. of positive electrons, N = no. of negative electrons.

* E. Q. Adams considers that the atomic weight of lead derived from actinium is 207. If this is the case all of the values for the actinium series should be recalculated.

The variation of N/P in a single series of atomic species may be exhibited by a consideration of the principal uranium, or radium, disintegration series. In order to secure increasing values in general, the series will be considered in the reverse order of disintegration, but without assuming at all that the nuclei could be actually built up in this way. Beginning with radium G, isotopic number 44, the value of N/P is 0.602. This decreases very slightly to 0.600 in the alpha addition to radium F, and then increases rapidly in two beta additions to 0.605 and 0.610. Then by one alpha addition it falls to 0.608, and by two beta additions rises to 0.612 and 0.617. Then in five alpha additions it falls to 0.615, 0.613, 0.611, 0.609, and 0.607, and by two beta additions rises to 0.612 and 0.617. Then in five alpha additions it falls to 0.614, the value for the principal isotope of uranium. There is thus in any series (in its reverse order) the same gradual fall of N/P in a series of alpha changes, as is found in the light elements when the atomic number rises and the isotopic number remains constant. In a beta addition in this region the increase of N/P is about 0.005, while among the light atoms a beta addition would increase the ratio much more markedly. Thus between $\mathrm{Ca}_0{}^{40}$ and $\mathrm{A}_4{}^{40}$ the increase per beta particle would be 0.025, or five times as great. It is obvious that in the actual disintegration of the radioactive elements the ratio *increases* by about 0.002 in an alpha disintegration, and *decreases* by about 0.005 in a beta disintegration. Thus UX_1 ($N/P = 0.616$) and RaB ($N/P = 0.617$) have about the same value of the ratio, since there are two beta and five alpha disintegrations between the two.

31. THE RELATIVE STABILITY OF RADIOACTIVE ISOTOPES AS RELATED TO THE RATIO OF NEGATIVE AND POSITIVE ELECTRONS IN ATOM NUCLEI.

According to an empirical rule discovered by Fajans the period (half life) of the atomic species in any set of isotopes decreases with falling atomic weight for species which undergo alpha disintegration, and increases with atomic weight for those which undergo beta disintegration. The second stability principle gives to this rule a theoretical form, as follows: *The greater the ratio* $\dfrac{\text{Total number of negative electrons}}{\text{Total number of positive electrons}}$ *in the nucleus the more rapid is a β-disintegration which lowers the ratio, and the less rapid is an α-disintegration which raises it, provided the net posi-*

tive charge on all of the nuclei considered is the same, that is, when isotopes alone are considered.[31]

According to Kossel[32] the Fajans rule is related to the number of cementing electrons in the nucleus, or more exactly to the value of f in the atomic weight equation of Harkins and Wilson in its simpler form:

$$P = 2(M + f).$$

It will be seen, however, that the relation to the ratio N/P is both simpler and more exact.

It will be seen that for any set of isotopes *the more positive the nucleus in the sense of the ratio P/N of positive to negative electrons, the more unstable it is with respect to the emission of positive alpha particles. Also the more negative the nucleus with respect to the ratio N/P of negative to positive electrons,*

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[31] The general idea on which the above relationship is based, is that as it becomes more negative in the sense that N/P increases, the nucleus binds positively charged particles more firmly, and negatively charged particles less firmly. While if isotopic atoms alone are considered, that is nuclei of constant net charge, there are only two complete exceptions to the relationship in about thirty-seven disintegrations, there is an apparent, but not actual, reversal of the rule when the nuclear charge varies. There are also three partial exceptions to the rule, in that members of the radium and actinium series of the same N/P ratio, have different periods, but this is to be expected as the result of more specific influences. These statements are based on the idea that the actinium series springs from U_{II}. Thus the reversal occurs in successive α-disintegrations, since as is well known, the period and, therefore, the stability of the nucleus, with reference to the giving off of α-particles, decreases rapidly as the disintegration proceeds. That is, as it becomes *less* positive, both with respect to its net charge and with reference to the ratio N/P, the nucleus holds each succeeding positive particle *less* firmly, so as the relative negative electron content increases, the stability with reference to the retention of positive α-particles decreases. In the radium series there are five, and in both the actinium and the thorium series as now known, four such successive α-disintegrations. There is also a reversal with respect to the loss of negative electrons, since the second β-disintegration is always more rapid than the first in the case of two successive changes of this nature, even though the nucleus is becoming more positive by the loss of its β-particles. There is thus an irregular, but periodic, variation in the stability of nuclei in any one series. As an hypothesis to account for this fact it has been suggested in an earlier paper that the negative cementing electrons are grouped in pairs, and that in the nucleus the α-particles are grouped in aggregates containing four or five (and probably other numbers, as low as one) such particles in each group, and that each aggregate becomes less stable as it decreases in size. (*Phys. Rev.*, **15**, 88 (1920)).

[32] Kossel: *Physik. Z.*, **12**, 265–9 (1919).

the more unstable it is with respect to the emission of negative beta particles.

The existence of the relation of Fajans is very strong evidence in favor of the idea that this ratio is of prime importance in determining the stability of atom nuclei. Other evidence of the same import will be found in the later sections on the abundance relations of the various atomic species. Since there are also other factors which are of extreme importance in determining stability, it is not to be expected that the Fajans relation will prove to be perfectly general; indeed, it seems remarkable that it holds at all exactly for atomic species which have descended from different ancestors, such as uranium and thorium. The great advantage of the radioactive evidence over that found by considering the relative abundance of the different atomic species, lies in the fact that the former includes information with respect to the type of instability involved.

32. THIRD, FOURTH, AND FIFTH STABILITY PRINCIPLES: THE HIGH RELATIVE FREQUENCY OF OCCURRENCE OF EVEN NUMBERS OF ELECTRONS AND PROTONS IN NUCLEI.

The third stability principle, already given, states that most atom nuclei contain an even number of negative electrons. The fourth principle is of somewhat less importance, and is based upon the statistical fact that there are many more atom nuclei and nuclear groups of electrons and protons, which contain an even number, than there are of those which contain an odd number of protons. As a stability principle this may be stated:

4. *Atom nuclei, and groups of protons and electrons in atom nuclei, are in general more stable when they contain an even, rather than an odd, number of protons.*

The fifth principle of stability is a combination of the third and the fourth, and has been extensively discussed in the first part of the present paper, where it was found that *elements of even atomic number are much more abundant than those of odd atomic number.*

5. Since most atom nuclei contain an even number (N) of negative electrons, and also most nuclei contain an even number (P) of positive electrons, it is evident that $P - N$ or M, the net positive charge on the nucleus must also be in general an even number, so *atoms whose net positive nuclear charge is an even number, are in general much more stable than when this*

charge is an odd number. Extensive evidence in support of this general relation will be found in Sections 12 to 18, inclusive, of the present paper. It may be recalled that in the meteorites elements of even atomic number are 70 times as abundant as those of odd atomic number.

Table XVII exhibits the remarkable fact that 94.6 per cent. of all of the atoms in the meteorites contain an *even number* of both nuclear *electrons* and *protons,* and so the net number of positive charges on the nuclei is also an even number.

TABLE XVII.

Atomic Percentage of the Atomic Species in the Meteorites (350 Stone to 10 Iron) in Which the Number of Nuclear Negative Electrons (N), of Protons (P) and of Net Charges on the Nucleus ($M = P - N$) is an Even Number.

Element.	Isotopic Number.	Atomic per cent.	P-N ($=M$)	P	N	N/P	Order of Abundance.
O	0	53.16	8	16	8	0.5	1
Si	0	13.82	14	28	14	0.5	2
Fe	4	11.76	26	56	30	0.536	3
Mg	0	9.86	12	24	12	0.5	4
Mg	2	1.65	12	26	14	0.538_5	5–6*
S	0	1.46	16	32	16	0.5	8
Fe	2(?)	1.03	26	54	28	0.518_5	10
Ca	0	0.95	20	40	20	0.5	11
Ni	2	0.50	28	58	30	0.517	13
Ni	4	0.26	28	60	32	0.533	14
Cr	4	0.13	24	52	28	0.539	15
Ti	4	0.005	22	48	26	0.542	20
Total	=	94.585 per cent.					

* Mg_2^{26} and Mg_1^{25} are present in about the same atomic percentage and are together fifth and sixth in order of abundance.

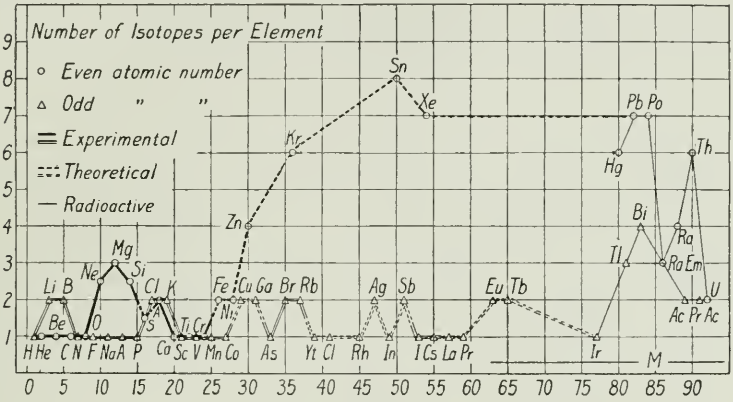
Thus the first four atomic species in order of abundance are all of the type represented by this table, and the fifth place is occupied by one of these together with another species of the same abundance.

The percentage of atoms in which the number of nuclear negative electrons is even, is higher than that given above by 2.1 per cent. or the total percentage is 96.7, while the percentage in which $P - N$ or M is even, is 98.

33. INDICATION OF THE FIFTH STABILITY PRINCIPLE THAT THERE ARE MORE ISOTOPES OF ELEMENTS OF EVEN THAN OF ODD ATOMIC NUMBER.

The hydrogen-helium theory, developed in 1915, indicated that there should be a marked difference in stability between the elements of even and of odd atomic number, and extensive evidence was presented to show that the atoms of the elements of even atomic number are much the more stable.[33] It is apparent that there should be more isotopes of those elements which have the more stable atoms, so it follows that there should be more isotopes of elements of even than of odd atomic number. That this is true for the radioactive elements was pointed out in 1917 by N. F. Hall.[34] A year earlier the writer[33] showed that the atomic weight relations give strong evidence that between atomic numbers 28 and 82 the number of isotopes is large. However, the above principle made evident that it was to be expected that *only the elements of even atomic number* would contain a large number of isotopes in this region.[35]

FIG. 11.



Several of the facts, which have now become known as the result of experiment, were pointed out earlier by the writer by the use of the general theory and the mean atomic weights. These were first, that the region of abundant isotopes would begin, for the even-numbered elements, at atomic number 28 or 30. Element 28 is the first element of even number in which the more abundant isotope has a lower atomic weight than the less abundant, and element 30, zinc, is the first in the series in which the number of isotopes rises to 4. It was also predicted that lithium and boron would be found to consist of two isotopes each, and thus in the limited section between atomic numbers 2 and 8 the number of isotopes is greater for elements of odd than for those of even number. This prediction was verified later by the experiments of Dempster, Thomson, and Aston.

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[33] Harkins: *Proc. Nat. Academy of Sciences,* 1, 186–214 (1916); *J. Am. Chem. Soc.,* 39, 856–79 (1917), and sections 12 to 16 of the present paper.

[34] Hall: *J. Am. Chem. Soc.,* 39, 1616–19 (1917).

[35] Harkins: *Ibid.,* 42, 1956–97 (1920). It is of interest that this idea that the isotopes of the elements of even number and not those of odd number in this region would be particularly numerous was contained in this paper, which was presented before the discovery of any isotopes in this region.

The validity of the general principle is exhibited clearly by Table XVIII and Fig. 11, which list the number of isotopes thus far found experimentally in this region.

TABLE XVIII.

Number of Isotopes of Elements of Atomic Numbers between 29 and 81.

Even Atomic Number.			Odd Atomic Number.		
Atomic Number.	Element.	Number of Isotopes.	Atomic Number.	Element.	Number of Isotopes.
30	Zinc	4	33	Arsenic	1
36	Krypton	6	35	Bromine	2
50	Tin	8	37	Rubidium	2
54	Xenon	7	53	Iodine	1
80	Mercury	7 (or 6)	55	Cæsium	1
	Total =	32			7
Average number	=	6.4			1.4

Thus there are 6.4 isotopes per element when the atomic number is even, and only 1.4 when it is odd, so far as the present data are concerned. *These results are a remarkable confirmation of the hydrogen-helium theory of the writer, since all of these relations were developed from the theory and the mean atomic weights before the discovery of the confirmatory evidence.*

34. THE NEW PERIODIC SYSTEM AS RELATED TO THE THIRD STABILITY PRINCIPLE.

In the periodic system of Mendelejeff, which relates to the properties of the outer atom, the number of elements per period is

2, 8, 18, and 32. In the new periodic system, which relates to the composition and stability of atom nuclei, the principal periodicity is of 2 units, which corresponds to the number of charges on the alpha particle, and there is a second periodicity of 4, corresponding to the mass of the alpha particles, but this second periodicity is much less apparent. It is evident that the third stability principle, which states that one of the most important of all stability conditions is that the most stable atoms contain an even number of negative electrons, indicates a periodicity of 2. It may be shown that this periodicity may be represented by a double network, such is exhibited graphically in Fig. 12, in which the abscissæ give the atomic, and the ordinates the isotopic numbers. Atomic and isotopic numbers which are even, are represented by heavy, while the odd numbers are represented by light lines. It will be seen that nearly all of the atomic species (46) lie at the junction of either the heavy lines, or else at the junction of the light lines, and that only very few (7) lie where heavy and light lines cross. Any atom represented by a point where heavy lines meet each other, or where light lines meet each other, contains an even number of nuclear negative electrons, while any atom at the junction of light with heavy lines contains an odd number of such electrons. The figure represents a limited part of that given in Fig. 9, which should be consulted for the general relations, but is on too small a scale to properly show the periodicity exhibited here, *which is that of periods of two along both axes; that is both with respect to the atomic and the isotopic numbers.* The isotopes which lie at intersections of heavy and light lines are not only less numerous, but on the whole they are less abundant than those which are at the intersection of lines which are alike.

The importance of the third stability principle is illustrated also by Table XIX, which lists the number of nuclear negative electrons in the most abundant isotope of each element thus far investigated by the positive ray method.

So far as present data indicate there are eight times as many elements in which the most abundant isotope contains an even number, as there are of those which contain an odd number of nuclear negative electrons.

TABLE XIX.

The Number of Negative Electrons in the Nucleus of the Most Abundant Isotopes of Each Element Thus Far Investigated by the Positive Ray Method.

Atomic Number.	Element.	Number (N) of Negative Electrons in the Nucleus.	
		Even Number.	Odd Number.
2	Helium	2	
3	Lithium	4	
4	Beryllium		5
5	Boron	6	
6	Carbon	6	
7	Nitrogen		7
8	Oxygen	8	
9	Fluorine	10	
10	Neon	10	
11	Sodium	12	
12	Magnesium	12	
14	Silicon	14	
15	Phosphorus	16	
16	Sulphur	16	
17	Chlorine	18	
18	Argon	22	
19	Potassium	20	
20	Calcium	20	
28	Nickel	30	
30	Zinc	34	
33	Arsenic	42	
35	Bromine	44	
36	Krypton	48	
37	Rubidium	48	
53	Iodine	74	
54	Xenon		75
55	Cæsium	78	

The above facts lead to the hypothesis that relative instability is the result of the presence of an odd number of negative nuclear electrons, either an instability of the nucleus, or an instability of the group containing the odd electron, this group being essential for the formation of the nucleus. In order to test this hypothesis we may turn to the radioactive atomic species (Table XX), where the stability of the nuclei is known in terms of their average periods of disintegration. It should be remarked that in considering nuclear instability mention should be made of the type of instability, which in the radioactive series would be instability with reference to beta particle emission.

TABLE XX.

Effect of an Odd Number of Negative Nuclear Electrons in Producing Nuclear Instability.

Atomic Species.	N (=even).	N = even Average Life.	N = odd Average Life.	N (=odd).	Atomic Species.
UX_1	144	35.5 days	1.65 min.	143	UX_2
$MeTh_1$	140	9.6 years	8.9 hours	139	$MsTh_2$
RaD	128	24 years	7.2 days	127	RaE

The above comparison indicates an extremely striking difference in each case between the periods, and shows that in each case the disintegration is much more rapid when the nucleus contains an odd number of electrons; about 50,000 times more rapid in the first case, 18,000 in the second, and 2200 in the third. The effect is not so striking in cases where there is a splitting of the series, but is in all cases in the proper order in the thorium and uranium series. It seems likely that in such a complex structure as the nucleus of a heavy atom there may be some exceptions to this general relationship, but none has been found thus far. Unfortunately, the atomic weight of none of the members of the actinium series is known, so the relations in that series cannot be listed. It is evident that they are not quite so simple as in the other two series.

35. HYPOTHESIS THAT THE NEGATIVE ELECTRONS IN ATOMIC NUCLEI, AND IN PROTON-ELECTRON GROUPS IN ATOM NUCLEI, ARE MOSTLY ARRANGED IN PAIRS.

When the above facts are taken into consideration, and especially since there seem to be two negative electrons in the alpha particle—the most important group in nuclear building—it seems that the following statement is justified: *The negative electrons in atom nuclei seem to be usually associated in pairs.*[36] This is not unlike the relation found by Lewis for the planetary electrons in molecules, since in only about one in a thousand molecules is there an odd number of planetary electrons. A later discussion will consider the relation of these pairs of nuclear negative electrons to the formula groups other than the alpha particle which seem to occur in the nucleus. The most prominent of these formula groups seem to be those of formulas p_3e_2 and p_2e_2, where p stands for a proton, and e for a negative electron. Both of these formula groups contain a single pair of negative electrons, just as is the case with the alpha particle.

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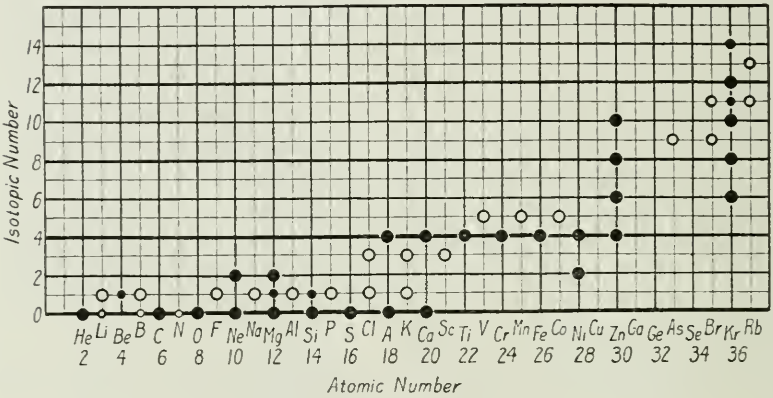
[36] Harkins: *Physical Review,* 15, 77 (Feb., 1920).

The rarity of atoms in which the number of negative nuclear electrons is odd is well illustrated by the meteorites. In no case does the average result of the quantitative analyses, as represented by any collected set of data, indicate the presence of any element whose most abundant isotope shows an odd value for N, and the only atomic species of this class which seem to be present are Mg_1^{25} (1.64 per cent.), and Si_1^{29} (about 1.5 per cent.) which together make up about 3 per cent. of the atoms of the material. Thus about 97 per cent. of the atoms have an even number for N. In the earth's crust, only about one atom in 50 has an odd value for N.

FIG. 12.



The new periodic system.

Possibly the most beautiful illustration of the effects of this tendency for N to be an even number is to be found in the atomic weights of the most abundant atomic species in each element of odd atomic number. When M is odd, since $P - N = M$, it is evident that either P or N, but not both, must be odd, so if, according to rule, N is even, then P or the *atomic weight must be odd.* Now it is very remarkable that the atomic weights of all of the elements from 3 to 27 inclusive, with the exception of nitrogen, are odd numbers, and the rule holds that P is odd for all of the individual isotopes as well, with the exception of those, such as B_0^{10} and Li_0^6, which occur only in extremely small percentages. The rule also holds for the isotopes found by Aston: Br_9^{79}, Na_1^{23},

Rb_{11}^{85}, Rb_{13}^{87}, Cs_{23}^{133}, K_1^{39}, K_3^{41}, Br_{11}^{81}, As_9^{75}, I_{21}^{127}, Cl_1^{35}, Cl_3^{37}, and possibly a Cl_5^{39}.

Additional evidence in favor of this hypothesis is found in the fact[36] that *whenever beta disintegrations of the radioactive atoms occur, there are usually two successive emissions of a beta particle, and in the remaining cases there is one beta emission just before, and a second just after, the ejection of an alpha particle.*

36. SECOND SYSTEM OF CLASSIFICATION OF ATOMIC SPECIES.

Before considering further the relation between nuclear stability and the isotopic number it is essential to outline a second method for classifying isotopes. This has already been suggested under the experimental correlations relating to the oddness or evenness of the numbers representing positive or negative nuclear electrons, and is given a definite form in Table XXI.

TABLE XXI.

Classification of Atomic Species According to Even and Odd Number of Electrons.

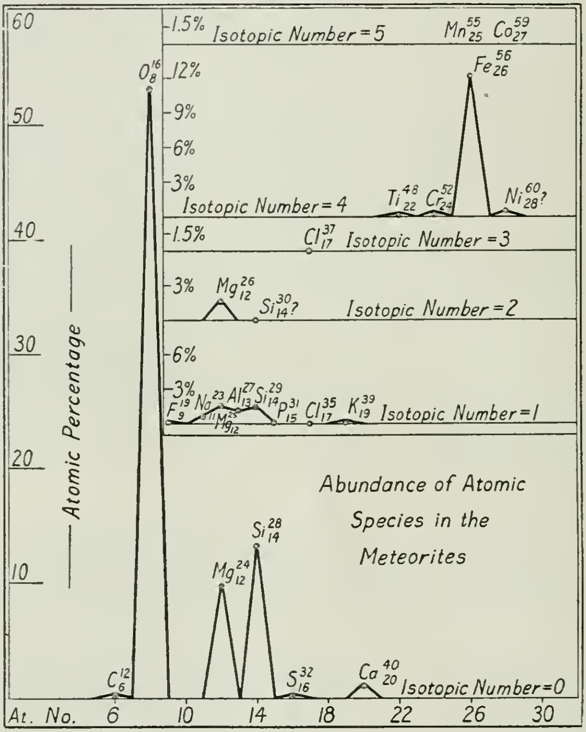
	Abundance in Atomic Percentage	
	Earth's Crust.	Meteorites.
Class I. $N =$ even, $P =$ even	86.9	93.2
Class II. $N =$ even, $P =$ odd	11.2	2.0
Class III. $N =$ odd, $P =$ odd	2.3	3.2
Class IV. $N =$ odd, $P =$ even	0.0	0.0

37. THE NEW PERIODIC SYSTEM AND THE ABUNDANCE OF ATOMIC SPECIES AS RELATED TO ISOTOPIC AND CLASS NUMBERS.

It is important to consider the N/P, M plot given in Fig. 10 as lying in a horizontal plane, while the abundance of the atomic species may be imagined to be represented by the vertical coördinates. On account of the difficulty of presenting such a three-dimensional figure, the data for the meteorites (Table XXII) are given in Fig. 13. This gives the third dimension for Figs. 5 to 10, and also 12. A similar plot for the crust of the earth (Table XXIII) is presented in Fig. 14.

The form of the three-dimensional plot may be imagined by supposing Figs. 13 and 14 to lie in a horizontal plane, but that the peaks which represent the abundance of the atoms are turned on the isotopic lines as axes until they stand vertically above the latter. While the isotopic lines are not equidistant in these figures this is due to the differences necessary to prevent a confusion of the peaks, so they should be imagined as spaced at equal distances. It should be remembered that since these two figures give the values for elements 2 to 30, they represent practically 100 per cent. of the material. The rectangle in the lower left-hand corner of Fig. 8 includes this region. Thus this rectangle includes all of the high peaks of abundance, while to the right and above this rectangle the peaks are so low as to be invisible

FIG. 13.



above the plane in a plot of ordinary dimensions. This is more apparent if it is considered that the total height of all of the several hundred peaks outside this rectangle, when added together (Fig. 8), is less than one five-hundredth of the height of the oxygen peak alone.

In Fig. 10 isotopic number 0 is represented by the X-axis, while all other values from 1 to 54 are represented by curves which have almost exactly the form of equilateral hyperbolæ. Along any of these curves the abundance of the isotopic species first rises and then falls. Thus, for example, on the curves for isotopic number 1, no atomic species are known above lithium (0.013 per cent. in the earth's crust). Going from this species downward toward the right the abundance increases to 0.030 for fluorine, 2.27 for sodium, 5.55 for aluminium, 1.22 for potassium, and beyond this no species are known. The figures for the meteorites are more in point, since they are affected less by segregation of the material, and the figures are: Lithium, boron, and fluorine not abundant enough to be given; sodium, 0.62; aluminium, 1.21; phosphorus, 0.06; potassium, 0.11; with no more species known. Oxygen, the most abundant species of isotopic number 0, and iron, the most abundant of isotopic number 4, are both near the middle of the general band of stability, and on the whole this is what may be expected, though individual stability influences may sometimes make a considerable shift in the position of the highest peak.

FIG. 14.

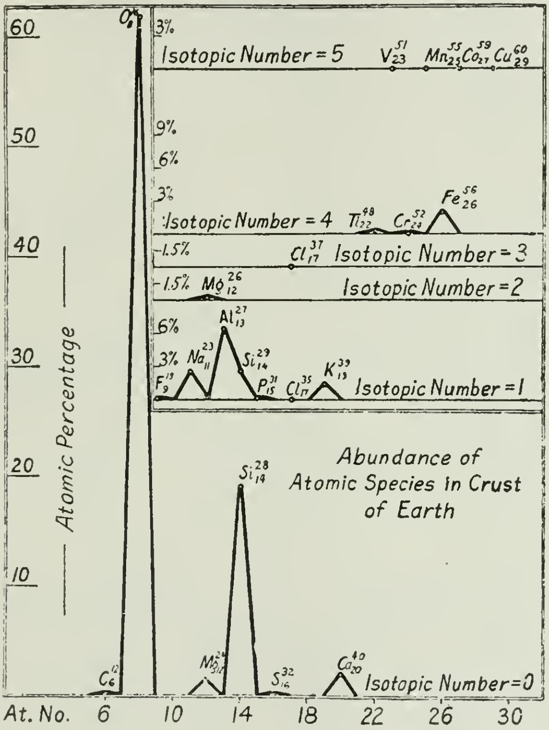


TABLE XXII.*

Abundance of the Atomic Species in the Meteorites as Classified According to Their Isotopic and Class Numbers.

(Atomic Percentage.)

Isotopic Number = 0.
Class Number = I.

Atomic Number.	Symbol.	Per cent.
6	C	0.12
8	O	53.16
12	Mg^{24}	9.86
14	Si^{28}	13.82
16	S	1.46
20	Ca	0.97
Total		79.39

Class Number = IV.

Atomic Number.	Symbol.	Per cent.
7	N	0.00

Isotopic Number = 1.
Class Number = II.

Atomic Number.	Symbol.	Per cent.
11	Na	0.62
13	Al	1.21
15	P	0.06
19	K	0.11
Total		2.00

Class Number = III.

Atomic Number.	Symbol.	Per cent.
12	Mg^{25}	1.65
14	Si^{29}	1.53
Total		3.18

Isotopic Number = 2.
Class Number = I.

Atomic Number.	Symbol.	Per cent.
12	Mg^{26}	1.65
14	Si^{30}	
28	Ni^{58}	0.50
Total		2.15

Isotopic Number = 3.
Class Number = II.

Atomic Number.	Symbol.	Per cent.
17	Cl	0.00
19	K	0.005
21	Sc	0.00

Isotopic Number = 4.
Class Number = I.

Atomic Number.	Symbol.	Per cent.
22	Ti	0.005
24	Cr	0.13
26	Fe^{56}	11.76
28	Ni^{60}	0.26
Total		12.93

Isotopic Number = 5.
Class Number = II.

Atomic Number.	Symbol.	Per cent.
23	V	0.00
25	Mn	0.06
27	Co	0.04
Total		0.10

It is worthy of note that the above percentages, together with that of the lower isotope of iron probably of isotopic number 2, whose percentage is not included, since it is uncertain as to its exact isotopic number, make up 99.9 per cent. of all of the material of the meteorites, and the similar atomic species, atomic numbers up to 28 and isotopic numbers—1 to 5, make up 99.9 per cent. of the earth's surface, which indicates that *no increase in the ratio of electrons to protons* (N/P) *is able to sufficiently stabilize atoms with a positive nuclear charge greater than 28 as to make such atomic species any considerable factor in the abundance relations. The important feature of this relation is that the abundance does not fall off gradually but suddenly, and remarkably enough the fall in abundance comes just beyond nickel, while nickel and zinc are the first of the elements in the region of abundant isotopes.* All abundant atomic species have isotopic numbers 4 or less.

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* Revised from a table given by the writer in *Phil. Mag.*, xlii, Sept., 1921, pp. 317 and 318.

TABLE XXIII.

Abundance of the Atomic Species in the Earth's Crust as Classified According to Their Isotopic and Class Numbers.

Isotopic Number = 0.
(N/P = 0.5.)
Class Number = I.

Atomic. Number.	Symbol.	Per cent.
6	C	0.047
8	O	61.94
12	Mg^{24}	1.40
14	Si^{28}	19.06
16	S	0.034
20	Ca	1.93
Total		84.41

Class Number = IV.

Atomic. Number.	Symbol.	Per cent.
3	Li^{6}	0.0005
5	B^{10}	....
7	N	....
Total		0.0005

Total Isotopic Number = 1 = 84.41

Isotopic Number = 1.
Class Number = II.

Atomic Number.	Symbol.	Per cent.
3	Li^{7}	0.009
5	B^{11}	0.00x
9	F	0.086
11	Na	2.64
13	Al	6.43
15	P	0.089
17	Cl^{35}	0.025
19	K	1.42
Total		10.70

Class Number = III.

Atomic Number.	Symbol.	Per cent.
12	Mg^{25}	0.22
14	Si^{29}	(?) 2.04
Total		2.26

Total Isotopic Number = 2 = 12.96

Isotopic Number = 2.
Class Number = I.

Atomic Number.	Symbol.	Per cent.
12	Mg^{26}	0.21
14	Si^{30}	?
26	(Fe^{54})	?
28	(Ni^{58})	0.01
Total		0.22

Isotopic Number = 3.
Class Number = II.

Atomic Number.	Symbol.	Per cent.
17	Cl^{37}	0.007
21	Sc	0.00000
19	K	0.07
Total		0.077

Isotopic Number = 4.*
Class Number = I.

Atomic Number.	Symbol.	Per cent.
22	Ti	0.28
24	Cr	0.017
26	Fe^{56}	1.88
28	Ni^{60}	0.005
30	Zn^{64}	0.000x
Total		2.19

Isotopic Number = 5.
Class Number = II.

Atomic Number.	Symbol.	Per cent.
17	Cl^{39}	.....
23	V	0.009
25	Mn	0.037
27	Co	0.000
29	Cu	0.0006 (?)
Total		0.047

Isotopic Number = 6.
Class Number = II.

Atomic Number.	Symbol.	Per cent.
30	(Zn^{66})	(0.0000x?)
32	(Ge^{70})	......
36	Kr^{78}	......

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* It should be noted that in isotopic number 4 the relations of isotopic number 0 are repeated, but with a much smaller abundance. Thus both have a high abundance relative to the adjacent atomic numbers; in both Class I is prominent, and while Class IV has not yet been found in isotopic number 4, it may be present, but only in a very minute quantity. Isotopic number 5 repeats in a lesser degree the relations of isotopic number 1, again with the omission of the secondary class, Class III. While the numbers given in the table may be changed slightly in a few cases by the discovery of new isotopes, the atomic weight and abundance relations indicate that *such changes will not affect the general relations* presented.

35. THE PERIODICITY OF FOUR WITH RESPECT TO THE ISOTOPIC NUMBER.

Fig. 13 exhibits the interesting relation that superimposed upon the periodicity of 2 with respect to the isotopic number as shown in Fig. 12, there is a periodicity of 4. This is shown plainly by Table XXIV.

TABLE XXIV.

Periodicity of 4 in the Variation of the Abundance of Atomic Species in the Meteorites with the Isotopic Number.

Isotopic Number.	Atomic Percentage.
0	79.39
1	5.18
2	2.15
3	0.005
4	12.16
5	0.10
6	0.000

While this periodicity may become obscured as the isotopic number increases, by the periodicity of 2 upon which it is superimposed, the table makes it evident that the former periodicity in abundance is very marked so long as the isotopic number is low. Fig. 12 shows that the number of isotopes also rises at isotopic number 4. The rise in abundance is very great between isotopic numbers 3 and 4; thus the abundance for isotopic number 4 is 2400 times what it is for the next lower number. Table XXIII shows that a similar table for the earth's crust would indicate a like periodicity, though the variation is not so marked, being represented by the factor 30 instead of 2400 between isotopic numbers 3 and 4. This illustrates what has been pointed out in other cases, that the chemical and physical segregation of the materials in the earth's crust makes all of the periodic relations less sharply defined than they are in the meteorites.

(*To be continued.*)

Rôle of Manganese in Plants.—J. S. McHARGUE, of the Kentucky Agricultural Experiment Station (*Jour. Am. Chem. Soc.*, 1922, xliv, 1592–1598), finds that manganese in conjunction with iron functions in the synthesis of chlorophyll. Manganese is therefore required by plants in order that they may assimilate carbon. Manganese possibly also plays a rôle in the synthesis of the proteins. Lack of manganese produces a chlorotic condition of the plant and cessation of growth.

J. S. H.

PRESENTATION OF THE FRANKLIN MEDAL AND CERTIFICATES OF HONORARY MEMBERSHIP,

MAY 17, 1922.

At the Stated Meeting of the Committee on Science and the Arts, held January 4, 1922, the following resolutions were adopted:

"*Resolved*, That The Franklin Medal be awarded to Dr. Ralph Modjeski, Civil Engineer, of New York City, New York, in recognition of his signal achievements as a designer and builder of structures, mainly bridges, many of them epoch-marking in the history of the engineering profession, beautiful as well as useful, involving on the part of the designer vision, courage and technic of the highest order."

"*Resolved*, That The Franklin Medal be awarded to Sir Joseph John Thomson, of Cambridge, England, in recognition of the immeasurable service he has rendered to the world as teacher and leader of thought in that domain of science especially related to a fundamental knowledge of electricity and the constitution of matter."

CORRESPONDENCE.

The Franklin Institute
of the state of pennsylvania
Philadelphia

office of the secretary

January 12, 1922.

Dr. Ralph Modjeski,
818 Widener Building,
Philadelphia, Pa.

Sir:

I have the honour to inform you that The Franklin Institute has awarded you The Franklin Medal, founded for the recognition of those workers in physical science and technology, without regard to country, whose efforts in the opinion of the Institute have done most to advance a knowledge of physical science or its applications. The award is minuted as follows:

> "That The Franklin Medal be awarded to Dr. Ralph Modjeski, Civil Engineer, New York City, New York, in recognition of his signal achievements as a designer and builder of structures, mainly bridges, many of them epoch-marking in the history of the engineering profession, beautiful as well as useful, involving on the part of the designer vision, courage and technic of the highest order."

The medal and accompanying certificate are being prepared, and I am requested, on behalf of our management, to extend to you a cordial invitation to come to the Institute on the afternoon of Wednesday, May 17th, to receive this medal and certificate from our President, Dr. Walton Clark.

I am

Respectfully,

(Signed) R. B. OWENS,

Secretary.

RBO: H

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818 Widener Bldg.,
Philadelphia, Pa.,
January 16, 1922.

DOCTOR R. B. OWENS, *Secretary,*
The Franklin Institute,
Philadelphia, Penna.

MY DEAR SIR:

I received your communication of January 12th and I wish to say that I consider the award of The Franklin Medal to me as the greatest honor that has ever been conferred upon me during my professional life.

I shall, of course, come to the Institute on the afternoon of Wednesday, May 17th, as requested. I shall then perhaps be able to express more fully my high appreciation of this award.

Very sincerely yours,

(Signed) RALPH MODJESKI.

RM MLS

THE FRANKLIN INSTITUTE
OF THE STATE OF PENNSYLVANIA
Philadelphia

OFFICE OF THE SECRETARY JANUARY 31, 1922.

Sir Joseph John Thomson, O.M., F.R.S., LL.D., Ph.D., D.Sc.,
Trinity College,
Cambridge, England.

SIR:

I have the honour to inform you that The Franklin Institute has awarded you The Franklin Medal, founded for the recognition of those workers in physical science and technology, without regard to country, whose efforts in the opinion of the Institute have done most to advance a knowledge of physical science or its applications. The award is minuted as follows:

> "That The Franklin Medal be awarded to Sir Joseph John Thomson, of Cambridge, England, in recognition of the immeasurable service he has rendered to the world as teacher and leader of thought in that domain of science especially related to a fundamental knowledge of electricity and the constitution of matter."

The medal and accompanying certificate are being prepared, and I am requested, on behalf of our management, to extend to you a cordial invitation to come to the Institute on the afternoon of Wednesday, May 17th, to receive this medal and certificate from our President, Dr. Walton Clark.

I am Respectfully,

(Signed) R. B. OWENS,

Secretary.

RBO: H

TRINITY LODGE, CAMBRIDGE,
March 1, 1922.

DEAR DR. OWENS:

Would you be kind enough to convey to the members of The Franklin Institute my grateful thanks for the signal honour they have paid me by conferring upon me The Franklin Medal. It is a great delight to me to receive a medal associated with the name of the Founder of Electrical Science. I wish I could come over to receive it, but I am obliged by statute as Master of the College to be in residence in term time so that the only times I am free are those when everybody is like myself, taking a holiday.

The pleasure the medal gave me has been enhanced by the fact that the announcement of it came from one whom I am proud to claim as an old pupil.

With very kind regards,
Yours very sincerely,
(Signed) J. J. THOMSON.

THE FRANKLIN INSTITUTE
OF THE STATE OF PENNSYLVANIA
Philadelphia

APRIL 4, 1922.

OFFICE OF THE SECRETARY

*Sir Auckland Geddes, Ambassador Extraordinary
and Plenipotentiary of His Britannic Majesty,
British Embassy, Washington, D. C.*

YOUR EXCELLENCY:

I have the honour to inform you that The Franklin Institute has awarded to Sir Joseph John Thomson, O.M., F.R.S., LL.D., Ph.D., D.Sc., Master of Trinity College, Professor of Physics, Cambridge University, England, The Franklin Medal, founded for the "recognition of those workers in physical science or technology, without regard to country, whose efforts in the opinion of the Institute have done most to advance a knowledge of physical science or its applications." The award is minuted as follows:

> "That The Franklin Medal be awarded to Sir Joseph John Thomson, of Cambridge, England, in recognition of the immeasurable service he has rendered to the world as teacher and leader of thought in that domain of science especially related to a fundamental knowledge of electricity and the constitution of matter."

The medal and accompanying certificate are being prepared, and I am requested, on behalf of our management, to extend to you a cordial invitation to come to the Institute on the afternoon of Wednesday, May 17th, to receive this medal and certificate from our President, on behalf of your Government, for Sir Joseph.

A second medal has been awarded to Dr. Ralph Modjeski, Civil Engineer. The award to him is minuted as follows:

> "That The Franklin Medal be awarded to Dr. Ralph Modjeski, Civil Engineer, New York City, New York, in recognition of his signal achievements as a designer and builder of structures, mainly

bridges, many of them epoch-marking in the history of the engineering profession, beautiful as well as useful, involving on the part of the designer, vision, courage and technic of the highest order."

It is hoped that it will be agreeable to you and to Dr. Modjeski to be guests of honour at a dinner to be given on the same evening by our President.

I am,

Your Excellency's very humble servant,

(Signed) R. B. OWENS,
Secretary.

RBO: H

BRITISH EMBASSY
Washington

APRIL 6, 1922.

DEAR SIR:

With reference to your letter of April 5th, enclosing the invitation of The Franklin Institute to Sir Auckland Geddes, I have to inform you that His Excellency is at present absent from Washington, but on his return on the 12th instant I shall not fail to bring to his attention your letter under reference.

Yours very truly,

(Signed) D. N. MACKEEN.

R. B. OWENS, ESQ., *Secretary,*
The Franklin Institute,
Philadelphia, Pa.

BRITISH EMBASSY
Washington

April 27, 1922.

DEAR MR. OWENS:

In confirmation of our telephone conversation of the other day, I have to inform you that events outside the control of the Ambassador will prevent his acceptance of your courteous invitation of the 5th. His Excellency will, however, be very glad to delegate one of the senior members of this Embassy to accept the medal on behalf of Sir Joseph Thomson in his place, and as soon as I know who is to go I shall inform you.

Yours sincerely,

(Signed) H. V. TENNANT.

R. B. OWENS, ESQ., *Secretary,*
The Franklin Institute,
Philadelphia, Pa.

Telegram from His Excellency Sir Auckland Geddes to Dr. R. B. Owens, Secretary, dated May 16, 1922:

Owing to unforeseen circumstances I have delegated Mr. R. L. Craigie, first secretary His Majesty's embassy, to receive Franklin Medal on May 17th in place of General Bethell. GEDDES.

STATED MEETING

WEDNESDAY, MAY 17, 1922

3.30 O'CLOCK

PROGRAMMME

PRESENTATION OF

THE FRANKLIN MEDAL

AND

CERTIFICATE OF HONORARY MEMBERSHIP

TO

MAJOR GENERAL H. K. BETHELL

C.B., C.M.G., C.V.O., D.S.O.
BRITISH EMBASSY
WASHINGTON, D. C.

ON BEHALF OF HIS BRITANNIC MAJESTY'S GOVERNMENT

FOR

SIR JOSEPH JOHN THOMSON

O.M., F.R.S., LL.D., PH.D., D.SC.
CAMBRIDGE, ENGLAND

PRESENTATION OF

THE FRANKLIN MEDAL

AND

CERTIFICATE OF HONORARY MEMBERSHIP

TO

RALPH MODJESKI, D.ENG.

NEW YORK CITY

PRESENTATION TO

THE INSTITUTE

OF A PORTRAIT OF

WALTON CLARK, M.E., D.SC.

PAPERS

ELECTRON THEORY OF SOLIDS

SIR JOSEPH JOHN THOMSON

O.M., F.R.S., LL.D., PH.D., D.SC.

READ BY JOSEPH S. AMES, PH.D., LL.D.

THE JOHNS HOPKINS UNIVERSITY

BALTIMORE, MARYLAND

BRIDGES—OLD AND NEW

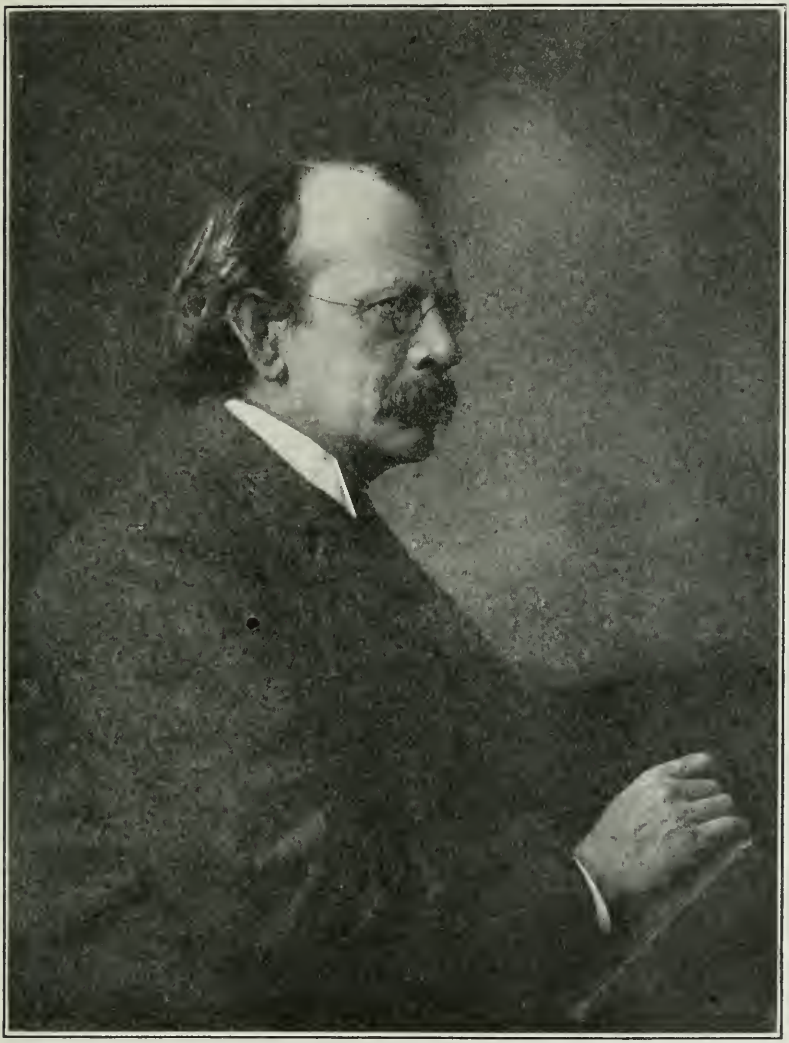
RALPH MODJESKI, D.ENG.

PRESENTATION OF THE FRANKLIN MEDAL AND CERTIFICATE OF HONORARY MEMBERSHIP TO DR. RALPH MODJESKI AND SIR JOSEPH JOHN THOMSON.

IN calling the meeting to order the President of the Institute announced that the business of the meeting would be the annual presentation of the Institute's highest award, The Franklin Medal, in recognition of distinguished scientific and technical achievements and recognized Dr. Joseph S. Ames, of the Johns Hopkins University, who made the following statement relative to the work of Sir Joseph John Thomson:

Mr. President: Your Committee on Science and the Arts, in its recommendations for the award of The Franklin Medals, has chosen two men whose names are known throughout the world. It is provided in the deed of gift that the medals shall be bestowed upon those " whose efforts, in the opinion of the Institute, have done most to advance physical science or its application." The first of these medals to be awarded to-day cannot, unfortunately, be handed directly to the recipient himself, since his duties at home make it impossible for him to be here. But we are honored by the presence of his fellow countryman, the official representative of Great Britain, who has graciously consented to accept, on behalf of his Government, The Franklin Medal awarded to Sir Joseph John Thomson, Master of Trinity College, Cambridge, and till recently Cavendish Professor of Experimental Physics. It is bestowed upon him in recognition of " the immeasurable service he has rendered to the world as teacher and leader of thought in that domain of science, especially related to a fundamental knowledge of electricity and the constitution of matter."

Sir Joseph John Thomson was born near Manchester in the year 1856, and received his early education in Owens College in



J. J. Thomson.

that city. From there he went to Cambridge and became a student at Trinity College, then, as now, the true home of men devoted to mathematics and physics. His career there was brilliant, as is shown by the number of prizes won and by the series of publications which then began. In 1880 he was Second Wrangler and also Second Smith Prizeman, being another of the long list of notable men who began their scientific lives with being Second Wrangler rather than first. His investigations, both theoretical and experimental, continued while he was Fellow of Trinity; and in 1884, when the Cavendish Professorship became vacant owing to the retirement of Lord Rayleigh, he was so obviously the man for this honored chair that he was urged, even by the Electors themselves, it is said, to become an official candidate. He was elected at once, and held the professorship until four years ago, thirty-four years of marvellous achievement. In 1918 he was elected Master of Trinity, and can now enjoy comparative leisure for his own studies.

His life has been marked by one honor after another. In 1884, the year he became Cavendish Professor, he was elected a Fellow of the Royal Society; universities and academies all over the world have honored him with degrees and election to their membership; in 1906 he was awarded the Nobel Prize—and, I may add, used the money which accompanies this award to supply the needs of the Cavendish Laboratory; and when the Order of Merit was instituted by the King he was one of those chosen as original members.

To all students of physics these honors bestowed upon Sir Joseph seem fit and proper. There is no living man to whom the science owes as much. He has profound mathematical insight and skill, an almost intuitive sense in directing the course of experimental investigation, but, above all else, imagination and fertility of suggestion. The progress in physics and chemistry, for which, in the history of science, the past forty years will always be distinguished, centres around our knowledge of atoms and molecules. Thomson's experiments on the discharge of electricity through gases and his theories of the structure of atoms were the beginning of all this work, carried on first at the Cavendish Laboratory and later in every physical laboratory in the world. Through all these years Thomson has ever been at the very fore of the advancing multitude. His brilliancy in making hypotheses to explain the facts revealed by experiments excites the admiration of every one, for they are hypotheses which bear fruit in further experiments. If any one requires abandonment or modification, he is ready with another which again guides the laboratory investigator. In the laboratory itself his work is directed by his unequaled knowledge of all the field of physics and lights the way for others. In addition to his personal services to science, he was, for the thirty-four years of his professorship, the director of the greatest physical laboratory in the world; a laboratory to which students from every country flocked. It was a delightful experience in those days to visit the Cavendish, as it was always called. In every room, in each corner of the room, there was an investigation in progress, often suggested by Thomson but always one with which he was familiar and to which he contributed much. In his own rooms he had his faithful Everett, a man of the greatest experimental skill, who received each day explicit directions and criticisms as to the fundamental work in which Thomson himself was engaged. If one looked far enough, it was discovered that the director did have an office, but what was notable was that its furniture consisted of a table and a stool, not a chair. Thomson would say that a chair tempted a man to sit down, while a stool inspired one to get up. As a lecturer in physics he, as a rule, talked about some mathematical problem in which at the time he was interested. His students were not men looking for degrees, but colleagues interested solely in advancing knowledge. With a group of men like that he could trust them to do their own reading and studying. No words can describe the full influence Thomson exercised upon his generation through his laboratory. The devotion of his associates was intense, there were affection and admiration. To everyone he was known as "J. J." Not that they addressed him as such, but whenever spoken of, then or now, no other name is used except this intimate one.

It would not be right to stop here with these general references to Thomson's services to science, without saying something of his part in the Great War. As the leading member of Lord Fisher's Inventions Board, all problems of a scientific nature were brought to him, and the help he rendered will never be known. I recall one incident which made a great impression upon me. You all remember Dürer's etching of the scholar in his study with a lion lying at the doorway, ready to give a hint to any intruding visitor. Thomson has no lion at his door; but he has a wife who performs the lion's duties. During the war I was spending a few days in Cambridge with Thomson on business. One Sunday morning Lady Thomson invited us into the garden to see her flower beds; we knew what that meant, of course. But while we admired the daffodils and the narcissi, I glanced in the library to see how Thomson did his work. There he was sitting deep down in an easy chair, his feet high on the mantlepiece, now and then running his fingers through his long hair—any one who knows him has seen him do it an hundred times—and that was all. No, he was not dreaming, he was not even smoking, he was thinking, thinking for the good of the British Empire and America. It was a picture full of meaning.

It is a cause of deep regret to everyone here that Thomson cannot be present to-day to receive in his own hands The Franklin Medal. Of all living physicists he is the best known personally to Americans. Many of my countrymen have been students in his laboratory, and he has been in this country several times, often for prolonged visits. He and Lady Thomson have exercised most generously the great gift of hospitality towards American visitors. But while we all deplore his absence, it is a subject of congratulation to ourselves that the Medal will be handed for temporary keeping to one who is highly appreciative of the service rendered to the fighting front by those who, like Thomson, put in the hands of the Allies means of unmeasured value with which to save modern civilization.

It gives me great pleasure, Mr. Chairman, to present to you Mr. R. L. Craigie, First Secretary of the British Embassy of Washington, who will receive The Franklin Medal and transmit it to Sir Joseph J. Thomson.

The Chairman then said:

I desire, Mr. Craigie, before proceeding with the presentation of The Franklin Medal—which is the business which has brought us here—to say to you and to our other guests that the members of The Franklin Institute are highly sensible of the distinction added to their meeting by the presence of a representative of the Government of Great Britain.

Mr. Secretary, I have the honor, in the name of The Franklin Institute, and upon the recommendation of its Committee on

Science and the Arts, to present to you, for transmission through the Foreign Office of your gracious sovereign to Sir Joseph John Thomson, The Franklin Medal and Diploma, and a Certificate of Honorary Membership in The Franklin Institute. This award is made to Sir Joseph in recognition of his distinguished services to mankind rendered in the field of science. It is the highest honor in the gift of the Institute.

Mr. Craigie, in accepting the Medal and Diploma and the Certificate of Honorary Membership, said:

Mr. Chairman, Ladies and Gentlemen: It is a great privilege to be present on this important occasion and to accept, on behalf of Sir Joseph John Thomson, the beautiful Medal and the Certificate of Honorary Membership which The Franklin Institute has bestowed upon him. To meet the members of this famous institution of learning is in itself an event which I prize highly. To accept from you a token of honor bestowed upon a scientist whom we hold in the highest esteem and for whom there is world-wide admiration marks the occasion as one of special significance.

The Franklin Medal is awarded " to those workers in physical science or technology, without regard to country, whose efforts, in the opinion of the Institute, have done most to advance a knowledge of physical science or its applications." Sir Joseph John Thomson has devoted to those very purposes a career which is full of enterprise and of valuable achievement and the fact that your choice should this year have fallen upon this distinguished physicist is not only, I know, deeply appreciated by him, but is regarded by his countrymen as a signal honor to the British Empire. His contributions to the advancement of those particular branches of science which he has made his own have been of incalculable value to his country and to the world. This recognition of his work by a distinguished American scientific body demonstrates once more that knowledge has no frontiers.

In this gathering of men of science I feel great diffidence in speaking of the achievements of science, but perhaps I may be permitted to refer to one aspect of scientific development which is of special interest to an Embassy and that is its influence on international relations. Behind all diplomacy lies the power to secure justice and that power must itself be based on knowledge and especially on those departments of knowledge which have been so much enriched by the researches and discoveries of Sir

Joseph John Thomson. In the great War, when you, and we, with all our allies, were called to defend freedom and the cause of right, we witnessed a most astounding development of the application of science to the methods of warfare. One of the most interesting instances of this development was in the department of optics which gave birth to the system of protective coloration, so largely utilized in the defense of vessels against submarines. Other applications of physical knowledge to submarine warfare spring readily to mind—the astonishing application of supersonic waves to determine the position of submarines, the use of electric detectors to indicate where and in what directions submarines were moving, or again in another field of military effort, the wonderful developments of sound ranging, or still again the almost incredible evolution of the science and art of flight in those few short years from August, 1914, to November, 1918. Here are perfect instances of the way in which knowledge created power in a moment of dire necessity.

Those were times of crisis, but the real, the great, the lasting achievement of science is not the aid it proffered in the day of battle, but the victories it wins for civilization and for peace. Inevitably, the war has left an aftermath of nationalism dangerously intense. Science, looking out on the world from its calm and exalted fastnesses, far removed from the dust of politics, should act as a corrective of that dangerous intenseness. The progressive advances of science are of world-wide concern and they so obviously transcend the limitations of frontiers that they seem to me to be capable of serving a most useful purpose in correcting the political perspective and in reminding us again, and yet again that we are a family of nations bound together by the closest ties of shared knowledge, the common basis of a common civilization. Directly and indirectly, science is called to play in the future an even greater rôle in the ceaseless struggle to preserve the world's peace.

The Franklin Institute, in awarding its medals independently of considerations of nationality, has taken a step which well illustrates the true relationship of science to the interests of mankind. Sir Joseph John Thomson has devoted his life to the work of adding rare precious stones to the walls of the rising temple of human knowledge, and it is with a feeling of gratitude and deep appreciation that His Majesty's Ambassador will forward this

Ralph Modjeski

medal of your award to the British Foreign Office for presentation to its distinguished recipient.

Doctor Onward Bates was then recognized and made the following statement concerning the work of Doctor Ralph Modjeski:

Mr. President: The Franklin Institute is known the world over as the promoter and guardian of physical science and its applications. Its policy is to encourage and to reward individuals who have done most in practically applying physical science to the benefit and use of mankind. On this occasion it honors an engineer who has made large contributions to the art of bridge building, through its action minuted as follows:

> "That The Franklin Medal be awarded to Dr. Ralph Modjeski, Civil Engineer, New York City, New York, in recognition of his signal achievements as a designer and builder of structures, mainly bridges, many of them epoch-marking in the history of the engineering profession, beautiful as well as useful, involving on the part of the designer, vision, courage and technic of the highest order."

This fair land in which we dwell has been marvellously blessed by divine providence. It is rich in natural resources which have been developed and used under favored conditions. Our citizens enjoy a degree of prosperity and comfort heretofore unknown, and when we seek the reason for this happy situation we find it is the providential outcome of science and industry. Of all the factors which enter into our civilization, facilities for transportation take rank among the first, perhaps are truly the first. Our country is enveloped in a network of railways, highways and footways furnishing the means of intercourse required in our manner of living and working. It would be difficult to overestimate the value to the nation of these different ways of communication. When the Delaware River Bridge is completed the people of Philadelphia will have practical evidence of the truth of this statement.

Engineers make roads, and in justice it must be added that they make some other things, and conversely, roads make engineers. Progress and experience go hand in hand and are reciprocal. Ours is a well-watered country, abounding with streams of all sizes, from rivulets to great rivers, all of which must be bridged when our people need roads across them. Rivers are the most formidable obstacles to be overcome in building roads. Some of the older ones in this audience may now remember the smallness of the great bridges of fifty years ago, and how in succeeding years the engineers kept on building bigger and better bridges, each in turn of greater span and magnitude, thus setting a new mark of possibility.

Engineers who accomplish "impossible" feats through their talents and energy receive but slight recognition from their fellowmen who do not grasp the marvels of the accomplishment, and who take the engineers and their work as a matter of course. It may also be stated that engineers are proverbially modest, of which we have evidence near at hand this very day. Nevertheless, engineers are human and desire appreciation as much as others do. When The Franklin Institute confers its highest honor on an engineer who ranks as a great bridge builder, it honors itself by the act which rewards him in a manner that will give him greater satisfaction than any other recognition it could offer him.

The award of The Franklin Medal to Ralph Modjeski will be approved by engineers as having been justly earned by him, and it will also be considered a tribute to his profession.

Doctor Modjeski is a man of distinguished ancestry with natural talents which would make him personally distinguished in many different lines of endeavor, if able to give them the requisite attention. His life, as will be observed in a statement following, has been devoted with energy and industry to the particular work of designing and constructing bridges. It is to be regretted that the present opportunity is too limited to present other than the abbreviated notes which follow:

BIOGRAPHICAL NOTES OF RALPH MODJESKI.

Born in Cracow, Poland, January 27, 1861. Father's name, Gustav Sinnmayor Modrzejewski. Mother's maiden name, Helena Opid. She changed her name for convenience to that of Modjeska upon becoming a citizen of the United States. She made her home in America and was known as a dramatic artist. She died in April, 1908.

Doctor Modjeski was naturalized an American citizen in 1883 when he took out final papers. He attended Grammar and High Schools in Cracow up to 1876, at which time he came to America with his mother. In 1878 he went to Paris, France, and attended the Government College "École des Ponts et Chaussees." Graduated with degree of Civil Engineer at the head of his class in

1885. Came to America that summer and received his first engagement with George S. Morison, Civil Engineer, as Assistant Engineer on construction of the Union Pacific Bridge at Omaha, Nebraska; remained with Morison in various capacities until 1892. During these seven years occupied the position of Assistant Engineer on the Omaha Bridge, from 1885 to 1887, Inspector in the shops for bridge work, 1887 to 1889 at Athens, Pennsylvania; later, Chief Draftsman in Morison's office in Chicago, 1889 to 1891. During this time, in charge of design of the Mississippi River Bridge at Memphis. In 1891, Chief Inspector at the shops for the Memphis Bridge superstructure. In 1892, Assistant Engineer of construction of the Memphis bridge. Early in 1893 opened an office in Chicago as Civil Engineer in independent practice.

The first large bridge designed and constructed by Doctor Modjeski was the government bridge at Rock Island, Illinois, over the Mississippi River, which is a double track railway and highway structure. Then followed the reconstruction of the Bismarck Bridge at Bismarck, North Dakota, over the Missouri River, and later the Thebes Bridge, over the Mississippi River at Thebes, Illinois. This bridge was built under the firm name of Noble and Modjeski, the late Alfred Noble was one of the partners. The bridge was commenced in 1903 and completed in 1905. Then came the Columbia River Bridge and Willamette River Bridge, both in Oregon, for the Spokane, Portland and Seattle Railway. These bridges, costing over $4,000,000, were commenced in 1905 and completed in 1908. Then came the McKinley Bridge over the Mississippi River at St. Louis, the Columbia River Bridge at Celilo, Oregon, for the Oregon Trunk Railway, as well as other bridges for that company, including a 340-foot arch over the Crooked River. Almost immediately after came the Broadway Bridge over the Willamette River in the City of Portland, Oregon.

The bridges more recently completed are the new double-track railroad and highway bridge at Memphis, Tennessee; the single-track railroad and highway bridge over the Mississippi River at Keokuk, Iowa; the Metropolis Bridge over the Ohio River, Metropolis, Illinois. On this last-mentioned bridge, employed as Consulting Engineer in preparation of designs in conjunction with the late C. H. Cartlidge until his death, when the bridge was turned over to Doctor Modjeski.

Consulting Engineer in charge of the new double-track railroad bridge over the Ohio River at Cincinnati, now under construction for the Cincinnati Southern Railway.

Consulting Engineer for the New York, New Haven and Hartford Railroad on their Thames River Bridge at New London, Connecticut, recently completed. In charge of reinforcing of the present Poughkeepsie Bridge over the Hudson River at Poughkeepsie. Member of the Board of Engineers, appointed by the Dominion Government of Canada for the reconstruction of the Quebec Bridge, the longest span in the world. Has been member of that Commission ever since its formation in 1908. Made a complete report for the New York Bridge Department on the strength of the New Manhattan Bridge in New York (1909). The Cherry Street Bridge at Toledo, Ohio, which is a concrete arch structure, was built under his direction and the plans previously prepared by other parties were modified by him. During his independent practice, he has acted as Consulting Engineer for various railways and corporations on smaller structures. Prepared two sets of standard plans of spans from 10 feet to 250 feet in length for the Northern Pacific Railroad. In 1916 was member of a Commission appointed by the Public Service Corporation of New Jersey to determine the feasibility of a vehicular tunnel under the Hudson River, including preliminary plans and estimates. Designed and constructed fireproof warehouse for the Rock Island Arsenal at Rock Island, Illinois.

The aggregate cost of the completed structures in the above list exceeds forty million dollars.

In addition to the above, he was appointed Chairman of the Board of Engineers to report on the location and prepare preliminary plans for a bridge between Philadelphia, Pennsylvania, and Camden, New Jersey. The bridge involves an expense of some $28,000,000. The report was completed on June 9, 1921.

In 1911 received an honorary degree of "Doctor of Engineering" at the University of Illinois. He is a member of the following societies: American Society of Civil Engineers, The Engineering Institute of Canada, British Institution of Civil Engineers, American Institute of Consulting Engineers, Past President and member of the Western Society of Engineers, Society for Promotion of Engineering Education, The Franklin Institute of

Philadelphia, French Association of Engineers, Former Student of École des Ponts et Chausses.

Member of the following clubs: Engineers' Club of New York, Past President of the Chicago Engineers' Club, which was organized on his initiative, Union League Club of Chicago, South Shore Country Club of Chicago, Cliff Dwellers Club of Chicago. Has offices in Chicago and New York.

Member of the firm of Modjeski and Angier, Civil and Inspecting Engineers, who also have offices in Chicago, New York, Pittsburgh and St. Louis.

Married in 1885 in New York; has three children, a daughter and two sons, one of whom was in the U. S. Army service during the war.

The list of some of Doctor Modjeski's works which for the sake of brevity have been read by name only, indicates many communities who may claim him as a citizen, but engineers are not restricted to localities—their citizenship lies where their talents are most needed, and on this occasion Doctor Modjeski is a Philadelphian.

Mr. President, the task assigned me of introducing this modest gentleman and great engineer has been poorly performed, but this is of little consequence in comparison with the pleasure I entertain in presenting to you, Ralph Modjeski.

The Chairman, in presenting The Franklin Medal, Diploma and Certificate of Honorary Membership to Doctor Modjeski, said:

Doctor Modjeski, I have the honor, in the name of The Franklin Institute, upon the recommendation of its Committee on Science and the Arts, and in recognition of your distinguished services to mankind rendered in the field of science, to present to you The Franklin Medal and Diploma, and a Certificate of Honorary Membership in The Franklin Institute. This award is the highest honor in the gift of the Institute.

Doctor Modjeski, in accepting The Franklin Medal and Diploma, and Certificate of Honorary Membership, said:

Mr. President, it is not possible for me to frame adequate words to express my appreciation of the two great honors which you are conferring upon me. The more I feel, the less I can say, so please just let me say I thank you.

The President then requested Mr. Coleman Sellers, Jr., Vice-

DR. WALTON CLARK.

President of the Franklin Institute. From a portrait by Lazar Raditz, presented to the Institute by its Board of Trustees, Board of Managers and Officers.

president of the Institute, to take the Chair. Mr. Sellers recognized Mr. Nathan Hayward, who in presenting a portrait of Doctor Walton Clark, President of the Institute, said:

Mr. President, Ladies and Gentlemen, it is my great honour to speak for the Board of Trustees, the Board of Managers, and Officers of The Franklin Institute, in presenting to the Institute this portrait of our President, Doctor Walton Clark.

It is not customary for those making a present to praise it, but we who have had the pleasure of arranging this gift are greatly pleased with the results obtained by the artist, Mr. Lazar Raditz. We feel he has done a masterly work in recording for us so pleasingly the features of a gentleman, scholar and friend. As Mr. Raditz has said to me, the subject is one affording a rare opportunity for the exercise of artistic effort.

It would indeed be a pleasure and a delight to review at this time Doctor Clark's work in developing the Institute along the lines laid down by its Founders, but I know that he does not wish this done. He is satisfied with results and these can be seen and enjoyed from day to day.

"In his own grace he doth exalt himself
More than in your addition."

Members of The Franklin Institute, I present in the name of the Board of Trusteees, Board of Managers, and Officers of the Institute this portrait as doing Doctor Clark the highest honour within our power to bestow, and as a token of the love and admiration of his fellow-workers.

Mr. Sellers, in accepting the portrait, said:

Mr. Hayward, it gives me profound pleasure to accept for The Franklin Institute of the State of Pennsylvania this admirable portrait of our distinguished President.

I am sure that I speak for all the members of the Institute when I say that they highly appreciate this gift and cordially thank the Trustees, Managers and Officers for their thoughtful generosity.

The portrait will not only be a highly valued addition to our collection, but it is a well-deserved tribute to Doctor Walton Clark who has guided the activities of this old Institution for the last sixteen years, with unselfish devotion and conspicuous success.

The President then took the chair and recognized Doctor Joseph S. Ames, of the Johns Hopkins University, who read the paper, "An Electron Theory of Solids," by Sir Joseph J. Thomson (page 281).

The President then recognized Doctor Modjeski, who read the paper on "Bridges—Old and New" (page 291).

CORRESPONDENCE.

THE FRANKLIN INSTITUTE
OF THE STATE OF PENNSYLVANIA
Philadelphia
OFFICE OF THE SECRETARY

May 24, 1922.

SIR AUCKLAND GEDDES,
Ambassador Extraordinary and
Plenipotentiary of His Britannic Majesty,
British Embassy, Washington, D. C.

YOUR EXCELLENCY:

Again you have put The Franklin Institute under a pleasing obligation. While expressing the regret of our Management that you were not able to be here on the afternoon of Wednesday, May 17th, last, to receive on behalf of your government The Franklin Medal recently awarded to Sir Joseph J. Thomson, Master of Trinity College, Cambridge, England, in recognition of his scientific work, I am particularly requested to advise you of the pleasure felt that the Embassy was represented by its distinguished Secretary, Mr. R. L. Craigie. Knowing something of the splendid traditions of His Majesty's diplomatic service, it is believed that your selection of Mr. Craigie was a most happy inspiration. His remarks on receiving the medal for transmission to Sir Joseph were graceful, highly pleasing to all scientific people, sound and constructive, distinctly promoting friendships that must continuously obtain if civilization is to progress.

Once more expressing to you the Institute's sense of indebtedness, I am,

Your Excellency's Very Obedient Servant,

(Signed) R. B. OWENS,
Secretary.

RBO:H

BRITISH EMBASSY,
Washington,
May 27, 1922.

MY DEAR DR. OWENS,

I am very much obliged to you for your letter of the 24th instant, and I was glad to hear from you that Mr. Craigie's remarks on receiving the Medal, for transmission to Sir Joseph Thomson, met with the approval of the Institute.

I very much regret that, owing to other engagements, it was impossible for me to be present on the 17th instant.

I am, my dear Dr. Owens,

Very sincerely yours,

(Signed) A. GEDDES.

DR. R. B. OWENS,
Secretary, The Franklin Institute,
Philadelphia, Pa.

BRITISH EMBASSY,
WASHINGTON,
August 15, 1922.

MY DEAR DR. OWENS:

I have received a despatch from the Foreign Office informing me that the Earl of Balfour presented The Franklin Medal to Sir J. J. Thomson on the 26th of last month. The ceremony, which took place at the Department of Scientific and Industrial Research in the presence of the United States Ambassador, the President of the Royal Society and other distinguished men of science, was highly successful. Sir J. J. Thomson made an excellent speech largely devoted to Franklin as a man of science. A newspaper extract is enclosed herein which will give you some further details regarding the ceremony.

The Earl of Balfour wishes me to say that it gave him great pleasure to take part in conveying to Sir J. J. Thomson the honour conferred upon him by his fellow scientists in the United States.

Very sincerly yours,

(Signed) H. G. CHILTON.

DR. R. B. OWENS,
Secretary, The Franklin Institute,
Philadelphia, Pa.
HG: I.

(*The Times* (London), Thursday, July 27, 1922.)

SIR JOSEPH THOMSON HONOURED.

BROTHERHOOD OF SCIENCE.

SIR JOSEPH THOMSON, O.M., F.R.S., yesterday received The Franklin Gold Medal, presented to him by The Franklin Institute, Philadelphia, " for signal and eminent service in science." The presentation was made by Lord Balfour at the Department of Scientific and Industrial Research, Old Queen-street, Westminster, and the ceremony was attended by many of the leading figures in the scientific world on both sides of the Atlantic.

LORD BALFOUR said that in honouring Sir Joseph Thomson The Franklin Institute had not merely conveyed a signal sense of their estimate of Sir Joseph's merits as an individual, but they had conferred an honour upon the country where he was born and where he had done all the great work that had given him the distinguised place he occupied without contest among the scientific celebrities of the world. He (Lord Balfour) was sorry to say he was old enough to remember the giants who rendered physics illustrious in this country in the second half of the nineteenth century. He knew Lord Kelvin well; he knew others of his great Cambridge contemporaries; and their fame was not likely to be shaken by any discoveries which their successors might be fortunate enough to make. Yet he thought he would be borne out by all those competent to speak when he said that the last decade of the last century and successive years of the twentieth century would always be remembered in the history of physical and mathematical science as some of the most fruitful and epoch making the world had ever known. (Cheers.)

Physical research had penetrated into regions never hitherto explored, and he well remembered that Lord Kelvin, who had himself done so much to prepare the new epoch, was nevertheless almost shocked by some of the theories which had now been accepted universally as representing the most recent advances in physical science. One of the greatest of pioneers in this greatest of scientific movements was Sir Joseph Thomson. (Cheers.) What he had done in physics, in electricity as a department of physics, in the structure of the atom, in all those investigations which were proving day by day more and more fruitful, which were opening up such astonishing and unimagined vistas into the truths of Nature, and the full importance of which only future generations would be able adequately to estimate—to all these great performances it would take far more time than they had at their disposal, and far more knowledge than he (Lord Balfour) pretended to possess, to do anyhing like justice.

SIR JOSEPH THOMSON said there was something besides a personal element in the bestowal of that honour—there was a contribution to the brotherhood of science between America and Britain. (Cheers.) He valued especially the association of the medal with the name of Franklin. He knew nothing quite analogous to Franklin's achievement in scientific history, for he obtained his immortal position practically by six years' work. He did it by sheer force of intellect, and he came to it without any scientific training. He had to the end of his life no mathematics. In fact, he was afraid Franklin classed mathematics and classics as things which it was quite undesirable to retain in a general scheme of education. (Laughter.) The writings of Franklin's contemporaries seemed out of date to-day, but not so Franklin's, and the striking thing about all his scientific work was that he appeared to regard it as a mere episode in his career to which he paid little importance. To find a man who had done work of the highest rank in so many subjects as Franklin, they had to go back to Leonardo da Vinci.

Among those present were:

Mr. H. Goold. representing the American Ambassador, Sir C. Sherrington (President), Sir David Prain (Treasurer), Mr. W. B. Hardy (Secretary), Sir Aubrey Strahan and Professor A. Harden, representing the Royal Society, Dr. Elwell Hendricks, representing the Society of Chemical Industries of New York and the American Chemical Society, Professor T. H. Goodspeed, Berkeley, U.S.A., Professor E. V. McCollum, Baltimore, U.S.A., Professor R. F. Ruttan, Canadian Advisory Council, and the following members of the Advisory Council of the Department of Scientific and Industrial Research: Sir William McCormick (Chairman), Professor J. B. Farmer, Sir George Beilby, Sir R. Threlfall, Professor S. Young, Sir J. F. C. Snell, Professor J. F. Thorpe, Sir H. Miers, and Sir H. Frank Heath (Secretary).

Milk Powders.—LEROY S. PALMER and C. D. DAHLE, of the University of Minnesota (*Jour. Dairy Science,* 1922, v, 240–245), have studied the structure of whole milk powders. Powders made by the spray process consist of spherical granules, each of which contains a spherical core of air. Powders manufactured by the drum process consist of irregular platelets free from cores of air. Spray process powders tend to deteriorate with the development of a strong tallowy odor; this deterioration is really an oxidation giving rise to rancidity. Drum process powders apparently do not undergo this deterioration. Palmer and Dahle suggest that the presence of the cores of air within the granules possibly has an important bearing on the deterioration of spray process powders. J. S. H.

Separation of Molybdenum from Tungsten.—DOROTHY HALL, of the Research Laboratory of the General Electrical Company (*Jour. Am. Chem. Soc.,* 1922, xliv, 1462–1465), recommends the following procedure for the quantitative separation of molybdenum from tungsten. Solid potassium xanthate is added to the neutral solution containing molybdenum and tungsten. Dilute (1:3) sulphuric acid is added drop by drop; the molybdenum is converted into its red xanthate; the tungsten is converted into soluble metatungstate, which may be reduced with the formation of a blue color. The solution is now shaken with chloroform, an immiscible solvent; the molybdenum xanthate passes into the chloroform layer, while the tungsten remains in the aqueous layer. This separation is most readily made when not more than 5 millegrams of molybdenum and not more than 1 gram of tungsten are present in the original solution.

J. S. H.

Manganese as an Industrial Poison.—GEORGE B. DAVIS and WALTER B. HUEY (*Jour. Ind. Hygiene,* 1921, iii, 231–238) report and describe two cases of chronic manganese poisoning. The men poisoned operated an electric furnace which was used for the melting of ferromanganese in a steel plant. J. S. H.

Industrial Carbon Monoxide Poisoning.—ALICE HAMILTON (*U. S. Bureau of Labor Statistics Bull. No. 291,* 47 pp., 1921) states that both acute and chronic carbon monoxide poisoning may occur in the industries. The acute poisoning may occur among workmen, employed in the steel, illuminating gas, and coke industries, coal and metal miners, zinc smelters, garage men, and those working in plants using producer gas. The chronic poisoning may develop when workmen are exposed to an atmosphere in which carbon monoxide is more or less continuously present in low concentrations; this condition may exist in garages and about linotype machines. J. S. H.

NOTES FROM THE U. S. BUREAU OF STANDARDS.*

MEASUREMENT OF THE COLOR TEMPERATURE OF THE MORE EFFICIENT ARTIFICIAL LIGHT SOURCES BY THE METHOD OF ROTATORY DISPERSION.[1]

By Irwin G. Priest.

[ABSTRACT.]

THIS paper describes and discusses a new method for measuring color temperatures between 3000° and 4000° absolute centigrade, and presents some data on the color temperature of the gas-filled tungsten lamp and the carbon arc.

The method is briefly this: Light from a source of known spectral distribution is modified by passage through a quartz plate between nicol prisms. The nicols and the quartz plate constitute in effect a blue filter of adjustable spectral transmission. The spectral transmission is adjusted by rotating one of the nicols. The source and the thickness of quartz are so chosen that the energy emerging from the second nicol has (for all positions to be considered) the spectral distribution characteristic of a complete radiator ("black body," Planckian formula). The light from the source whose color temperature is to be determined is color matched by rotating one of the nicol prisms. The temperature is obtained from this rotation by a method described in the paper.

The subject matter includes:

(1) A thorough discussion of the reliability of the standard source.

(2) Data upon the precision and accuracy of color temperature measurements at about 2850° K. It is shown that the probable error of a single observation is about ∓6°. Individual observers means (20 observations) differ from the mean of four observers by about 5°.

(3) Data upon the color temperature of the gas-filled tungsten lamp as a function of efficiency up to nearly the melting

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* Communicated by the Director.

[1] Scientific Paper No. 443.

point of tungsten. The filament failed at a temperature of about 3644° K., the efficiency being about 39 lumens per watt.

(4) Data upon the color temperature of the crater of the carbon arc indicate a color temperature of about 3780° K. for solid carbons and 3420° K. for cored carbons.

PRACTICAL SPECTROGRAPHIC ANALYSIS.[2]

By W. F. Meggers, C. C. Kiess and F. J. Stimson.

[ABSTRACT.]

A brief review of various methods which have been proposed for chemical analyses by means of the spectrum is followed by a detailed description of the principle, apparatus and procedure employed in making quantitative analyses from the spectra of condensed sparks. The principle is based on the well-known fact that if one examines the spectra of flames, arcs or sparks, either visually or photographically, it is seen that with the diminution of an element in a mixture its spectrum becomes simplified, more and more lines disappear, so that in general only one extremely sensitive line remains when a minute trace of the element is present. From a study of standard samples whose chemical composition is known, the partial spectrum of each element may be correlated with the amount present, thus furnishing a basis for estimating the composition of impure materials. Such tests have the widest application and are best controlled and interpreted when the materials are made luminous in a high potential capacity spark and the spectra of standard and unknown samples are photographed for comparison. The practical application of this method is illustrated by three examples taken from the work of the spectroscopy section of the Bureau of Standards. They deal with the quantitative determination of impurities in various samples of tin, gold and platinum. This spectrographic method of analysis is especially sensitive and useful in nearly all cases where small quantities of samples or impurities are to be tested and can therefore be used to advantage in supplementing assays or the wet methods of chemical analysis which in many such cases are difficult and uncertain. For routine work of this nature a standardized spectrographic method will furnish results of consider-

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[2] Scientific Paper No. 444.

able accuracy and will reduce the time and expense involved by the more tedious methods. Other applications to problems in chemistry, metallurgy, mineralogy, physics, biology, etc., are suggested.

PHOTOMICROGRAPHY OF PAPER FIBRES.[3]

By R. E. Lofton.

[ABSTRACT.]

IT IS necessary that persons who intend taking up the subject of photomicrography make themselves thoroughly familiar with the laws and properties of light and lenses, the proper use of the microscope, and with the nature and properties of developers and the photographic plate.

It is not necessary, and is even a disadvantage, to have the illumination furnished by the carbon arc, which may be advantageously replaced by an incandescent lamp having a concentrated filament. The writer is using with entire success a 400-watt 110-volt Mazda stereopticon lamp, and has thus eliminated a cause of periodic diversion of attention from the object being studied and also a source of heat which frequently injures or destroys valuable equipment or delicate objects being photographed.

Achromatic objectives cannot be corrected for all wave-lengths of ordinary light, but are corrected for " apple green " light when intended for visual use, since the normal human eye is most sensitive to light of this color. But since all photographic plates are more sensitive to the blue-violet waves, objectives intended for photographic use are corrected for blue light. The color of light for which the objective is corrected is brought to a focus nearer the objective than are the other colors of the spectrum, so it follows that the visual focus and the photographic or chemical focus are not located at the same point. In the use of achromatic objectives, therefore, with ordinary light it is necessary for best results to use a light filter between the objective and source of light to " cut out " or absorb the colors of light not desirable. If the objective to be used is corrected for visual use, best results will usually be obtained if a filter is used which transmits only the yellow-green; but if the objective is corrected for photographic use, the filter used with it should transmit only blue light.

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[3] Technologic Papers, No. 217.

Apochromatic objectives, however, are corrected for all the components of white light, and thus bring to the same focus both the visual and the chemical rays, so that it is not necessary to filter the light when using them with compensating oculars. But if one wishes to use an apochromatic objective without a compensating ocular it will be necessary to use monochromatic light, as this objective is so constructed that it will not give an image free from color, if ordinary light is used, except in combination with a compensating ocular.

Three types of filters are in common use: (1) Liquid filters (dyes in solution), (2) those made of colored glass, and (3) stained or dyed transparent films. Liquid filters do not usually keep well and are apt to be spilled and do damage. Those in the other two classes are in general much more satisfactory. A very satisfactory filter can often be made in the workroom by removing the silver salts from a photographic plate and staining the clear gelatin film in a dye bath. Filters may be examined quickly for the quality of light they transmit by means of a grating or a replica.

In using objectives of 8 mm. or greater equivalent focus a regular substage condenser is not desirable, as better results can usually be obtained with a condenser arrangement which sends a narrow parallel beam of light into the objective.

A substage diaphragm should be used, especially if a condenser of high numerical aperture is being used. A very small diaphragm should not be used in any case, as diffraction effects with consequent loss of resolution are sure to result.

If the object to be photographed lies in slightly separated planes vertical to the axis of the optical system, an objective of longer focal length, since it has greater "penetrating power," will give better results than one of shorter focal length. An objective of greater focal length also gives a larger and a flatter image. At the same time a longer bellows extension must be used by which means the image to be recorded on the photographic plate will be as free as possible from curvature and will show most detail in the object.

The proper plate to use will depend on the color and the other properties of the material to be photographed; but whether an ordinary, orthochromatic, or panchromatic plate is to be used, best results can be had only by the use of a fairly slow plate. Development should be carried out with a strong solution, so that plenty of contrast will appear in the finished negative.

It is very important that the microscopist be familiar with the characteristics of the fibres to be photographed, and that a field be selected for photographing which will show the distinguishing properties and the correct proportion of all the fibres or cells composing the sample.

The use of stains and dyes has the advantage of aiding in identifying various fibres by bringing to view characteristic markings and by having different staining effects on different fibres and on different elements of the same fibre. By slight staining of the fibres the gray background so often seen in reproductions of photomicrographs may be eliminated.

Photomicrography affords a rapid, inexpensive, and accurate means for preparing permanent records in the study of the quality, adulteration, or deterioration of raw materials and in the control of various mill processes.

CONSTRUCTION AND OPERATION OF A TWO-CIRCUIT RADIO RECEIVING EQUIPMENT WITH WITH CRYSTAL DETECTOR.[4]

[ABSTRACT.]

THE apparatus used for the reception of radio messages may be a homemade affair, very simple and inexpensive, or it may be elaborate and expensive. All that is necessary for receiving radio messages is a device for collecting power from incoming radio waves, a suitable circuit adjusted or " tuned " electrically to the frequency of the incoming waves, and apparatus for changing the received power into audible sounds.

Bureau of Standards Circular No. 120, " The Construction and Operation of a Simple Homemade Radio Receiving Outfit," described the method of constructing in the home a very simple and inexpensive single-circuit crystal detector receiving set from materials which can be easily secured. Circular No. 120 was the first of a series of circulars describing the construction of homemade radio receiving sets. The publication of these circulars was undertaken by the Bureau of Standards at the request of the States Relation Service of the United States Department of Agriculture acting in coöperation with the Bureau of Markets and Crop Estimates of the same Department.

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[4] Circular No. 121.

The Circular here described is the second of this series, and gives directions for the construction of a more elaborate receiving set, having two circuits instead of a single circuit. This set has a variable condenser, and a coupling coil by means of which variable coupling may be secured. With this set more selective reception may be obtained, that is, stations which it is not desired to receive can be tuned out, and stations which it is desired to hear can be heard better. The set has more adjustments than the one described in Circular No. 120.

In the construction of the two-circuit receiving outfit, the antenna, lightning switch and ground connections described in Bureau of Standards Circular No. 120 can be used. The receiving set itself consists of two separately tuned circuits, a crystal detector, and telephone receivers. The total cost of the complete equipment will vary from about $15.00 to $24.00. If one has constructed the equipment described in Circular No. 120, the cost of additional parts required to construct the equipment described in this Circular will be from $3.00 to $8.00.

The complete receiving station is divided into the following parts: (1) Antenna, (2) lightning switch, (3) ground connections, (4) receiving set, and (5) telephone receivers. The receiving set may be subdivided into (1) the coupler (with its variable tuning condenser) and (2) the crystal detector.

The "means of absorbing the energy from the waves" is the antenna, the "means of tuning" consist of the coupler and variable condenser, and the "means of making audible the high-frequency radio currents" consist of the detector and telephone receivers.

The antenna may be a wire 75 feet long between insulators which are attached to buildings or other convenient supports.

The lightning switch is a single-pole double-throw porcelain base switch, and is so connected that the antenna may be grounded when not in use.

The coupler has a "primary" and a "secondary" coil. The primary coil is made a part of the electrical circuit between the antenna and ground. The coil is made by winding insulated wire on cardboard tubing and the desired number of turns is controlled by switches which tune the primary circuit to the desired wave frequency. The secondary coil is similar to the primary coil except that the number of turns is controlled by a single switch. This coil, which is slightly smaller in diameter than the primary, is arranged so that it may be pushed into the latter, and the terminals of the coil are connected to a variable condenser so that the complete secondary circuit may be tuned to the frequency of the primary circuit. When this occurs there is a transfer of energy between the two circuits, and the signals are made audible by a crystal detector and telephone receivers. The detector is made by mounting a tested piece of the mineral galena so that it is in contact with a fine wire. The telephone receivers must be purchased, and although a single telephone receiver may be used, it is more desirable to use two telephone receivers having a combined resistance of 2000 ohms or more.

The equipment described in this Circular will receive music and voice from high-power radio telephone transmitting stations from a distance of about 75 miles, and will receive stations of lower power over a distance of about ten miles. Much greater distances may sometimes be covered at night.

THE SPECTRAL TRANSMISSIVE PROPERTIES OF DYES.

By K. S. Gibson, H. J. McNicholas, W. E. Mathewson, E. P. T. Tyndall, and M. K. Frehafer.

[ABSTRACT.]

I. Of Seven Permitted Food Dyes in the Visible, Ultra-violet, and Near Infra-red.[5]

THE paper presents the beginning of an extended investigation of the spectral transmissive properties of dyes. The purpose of this first paper is (1) to outline the scope of the work, (2) to describe the apparatus and methods used, and (3) to present the data already obtained.

Owing to the arbitrary conventions in nomenclature, symbols, and units heretofore employed, it has seemed advisable to formulate a complete system of nomenclature for the subject, part of which is presented in this paper. In this system, *Transmittancy* is defined as the ratio of that fraction of the incident

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[5] Scientific Papers, No. 440.

radiant energy which is transmitted by a cell containing the solution, to that fraction of incident energy of the same intensity which is transmitted by the same or a duplicate cell containing the solvent. It is the quantity obtained directly from the observations. *Specific Transmissive Index* equals *$-Log_{10}$ Transmittancy* for unit concentration and thickness. The units employed are 1 cg. per litre and 1 cm. respectively.

The experimental data are presented in the form of graphs and tables. The *graph* forms are of two kinds: (1) with *$-Log_{10}$ Transmittancy* from 0.00 to 2.00 as ordinates and *Wave-length* in millimicrons from 390 to 770 as abscissæ; (2) with ordinates the same as above and having as abscissæ the *Frequency* in vibrations per 10^{-12} seconds from 300 to 1300. The *tables* give the specific transmissive index for homogeneous light of various wave-lengths, from mercury and helium lamps, throughout the visible spectrum, and the values of index and frequency (and wave-length) of the maxima and minima of the absorption bands throughout the whole range.

Four methods were used to obtain the experimental data:

(1) *Visual Method.*—The König-Martens polarization spectrophotometer was used. (*Ann. der Phys.* (4) 12, p. 985, 1903.) Auxiliary apparatus for illuminating the spectrophotometer field is partially described in B. S. Technical Papers, No. 148. This method was used in the range of wave-lengths 436 to 710 millimicrons.

(2) *Photographic Method.*—The Hilger sector photometer with a quartz spectrograph was used over the wave-length range of 240 to 500 millimicrons. The source of radiant energy was a high-voltage (Tesla coil) spark under water, which gives a continuous spectrum throughout the visible and ultra-violet as far as the quartz system will transmit.

(3) *Photoelectric Null Method.*—This method and apparatus are fully described in B. S. Sci. Papers No. 349. A Hilger constant-deviation spectrometer with glass prism and lenses was used. Because of the absorption by the glass in the ultraviolet, and of the long wave-length limit of sensitivity of the potassium-hydride photoelectric cells, the range of practical use of this method was limited to 380 to 600 millimicrons. It has its

maximum sensitivity, however, in the blue where the visual and photographic methods are relatively weak.

(4) *The Thermoelectric Method.*—The calibration of the drum of the Hilger constant-deviation spectrometer was extended into the near infra-red, enabling the instrument to be used throughout the range in which 1 cm. of water has any appreciable transmission. The radiometric apparatus consisted of a thermopile and galvanometer, and the usual deflection method was used. The approximate wave-length range of the method was 600 to 1360 millimicrons.

The absorption cells were so constructed that the solution came in contact with glass or quartz only, and were kept at a constant temperature by means of a water bath regulated by a thermostat.

The data as actually obtained by the different methods are plotted on the graph forms, and as the wave-length ranges of the different methods overlap to a considerable extent, these graphs afford a means of thoroughly studying the accuracy of measurement attainable with these various instruments and methods. Systematic errors have in this way been studied and, as far as possible, eliminated, so that very good agreement between methods is attained.

The dyes investigated were seven of the permitted food dyes—Naphthol-Yellow S, Orange I, Ponceau 3R, Amaranth, Erythrosine, Indigo Disulpho Acid, and Light Green SF Yellowish. It was desired to obtain the data on these substances in pure water solution. They all, however, show the properties of indicators, and as ordinary distilled water may show considerable variation in its H-ion concentration, a sufficient quantity of a salt-mixture regulator was added to fix the acidity of the solvent within somewhat narrower limits. Erythrosine, however, was dissolved in pure distilled water.

Concentrations of 1, 10, 100, and 1000 centigrams per litre, thicknesses of 1, 2, 4, and 10 centimetres, and temperatures of 25 and 40° C., were used. Deviations from Beer's law were noted; and also temperature effects.

An inspection of the graphs and tables must be made by those interested, inasmuch as this kind of data is not readily summarized.

WAVE-LENGTH MEASUREMENTS IN THE ARC SPECTRA OF NEODYMIUM AND SAMARIUM.[6]

By C. C. Kiess.

[ABSTRACT.]

THE arc spectra of neodymium and samarium were photographed with a large concave grating spectrograph, the photographic plates being suitably sensitized to record the spectra from the green to the infra-red. About 1500 lines were measured in each spectrum, most of them being of low intensity. No bands were observed in either spectrum, although a few unsymmetrical lines may be regarded as band heads. About 125 lines common to both spectra have been segregated into a separate table. These lines may be characteristic of the element of atomic number 61 which comes between neodymium and samarium, but which has not yet been isolated. The materials used for the work were neodymium oxalate and samarium oxide prepared at the University of Illinois and samarium oxalate prepared at New Hampshire College. This work is a continuation of a study of the spectra of the rare earth elements of which a first report is given in B. S. Scientific Papers, No. 421.

UNITED STATES GOVERNMENT SPECIFICATION FOR WHITE FLOATING SOAP.[7]

[ABSTRACT.]

THIS specification was prepared by a technical committee of the Federal Specifications Board in coöperation with the Soap Committee of the Soap Section of the American Specialty Manufacturers' Association, and was promulgated by the Federal Specifications Board on June 20, 1922. The specification gives the general requirements and detailed methods of sampling and testing, the preparation of the reagents required, and the basis of purchase. The methods of sampling and testing were prepared by a committee of the American Chemical Society in coöperation with the two committees mentioned above. The general requirements are:

The soap desired under this specification is a high-grade cake soap, at least as good in every respect as one made from soda and a mixture of high-grade tallow with 25 to 30 per cent. of coconut

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[6] Scientific Papers, No. 442.

[7] Circular No. 123.

oil; of good light color; thoroughly saponified; so prepared as to float on water. Bidder shall state size, weight and number of cakes in each box.

Failure to meet any of the following requirements will be cause for rejection:

Matter volatile at 105° C. shall not exceed 34 per cent. Deliveries which yield more than 34 per cent. volatile matter will be rejected without further test.

The sum of free alkali, total matter insoluble in alcohol and sodium chloride shall not exceed 2.0 per cent.

Free alkali, calculated as sodium hydroxide (NaOH), shall not exceed 0.15 per cent.

Chloride, calculated as sodium chloride (NaCl), shall not exceed 1 per cent.

Matter insoluble in water shall not exceed 0.2 per cent.

Rosin, sugar and foreign matter shall not be present.

The acid number of the mixed fatty acids prepared from the soap must be not less than 212.

Odor and character of cake must be as specified by the purchaser.

The percentage of matter volatile at 105° C. will be computed on the basis of the soap as received but all other constituents will be calculated on the basis of material containing 28 per cent. of volatile matter.

The material will be purchased by net weight, provided the matter volatile at 105° C. does not exceed 28 per cent. With deliveries containing more than 28 per cent. but not exceeding 34 per cent. of matter volatile at 105° C., settlement will be made on the basis of 28 per cent. of matter volatile at 105° C., *i.e.*, seventy-two one-hundredths (72-100) of a pound of non-volatile matter shall be considered one (1) pound of soap.

UNITED STATES GOVERNMENT SPECIFICATION FOR LIQUID SOAP.[8]

[ABSTRACT.]

THIS specification was prepared by a technical committee of the Federal Specifications Board in coöperation with the Soap Committee of the Soap Section of the American Specialty Manufacturers' Association, and was promulgated by the Federal

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[8] Circular No. 124.

Specifications Board on June 20, 1922. The specification gives the general requirements and detailed methods of sampling and testing, the preparation of the reagents required, and the basis of purchase. The methods of sampling and testing were prepared by a committee of the American Chemical Society in coöperation with the two committees mentioned above. The general requirements are:

The soap desired under this specification is a clear solution of pure vegetable oil potash (or potash and soda) soap with or without glycerol or alcohol, suitably perfumed and free from all foreign matter. It should quickly form a satisfactory lather and have no injurious effect, and leave no objectionable odor on the skin.

Bidder shall state number of gallons to the container.

Failure to meet any of the following requirements will be cause for rejection:

The material must be a clear solution, free from objectionable odor, other than from coconut oil, and must quickly form a satisfactory lather.

Total anhydrous soap shall be not less than the equivalent of 15 per cent. potash soap.

Total matter insoluble in alcohol shall not exceed 0.5 per cent.

Free alkali calculated as potassium hydroxide (KOH) shall not exceed 0.05 per cent.

Chloride calculated as potassium chloride (KCl) shall not exceed 0.3 per cent.

More than traces of sulphates and sugar shall not be present.

All constituents shall be calculated on the basis of the original sample.

The material will be purchased by volume in accordance with the contract agreement. A gallon of soap shall mean 231 cubic inches at 15.5° C.

UNITED STATES GOVERNMENT SPECIFICATION FOR SOAP POWDER.[9]

[ABSTRACT.]

THIS specification was prepared by a technical committee of the Federal Specifications Board in coöperation with the Soap Committee of the Soap Section of the American Specialty

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[9] Circular No. 125.

Manufacturers' Association, and was promulgated by the Federal Specifications Board on June 20, 1922. The specification gives the general requirements and detailed methods of sampling and testing, the preparation of the reagents required, and the basis of purchase. The methods of sampling and testing were prepared by a committee of the American Chemical Society in coöperation with the two committees mentioned above. The general requirements are:

The material desired under this specification is a uniform mixture of soap and sodium carbonate in powdered form; it should be readily soluble in tepid water and should contain no free caustic alkali or inert fillers.

Bidder shall state size and number of pounds to the package.

Failure to meet any of the following requirements will be cause for rejection:

Anhydrous soap shall be not less than 15 per cent.

Sodium carbonate (Na_2CO_3) shall be not less than 30 per cent. (The aggregate of anhydrous soap and sodium carbonate shall be not less than 55 per cent.)

Material will be purchased by net weight.

UNITED STATES GOVERNMENT SPECIFICATION FOR SALT WATER SOAP.[10]

[ABSTRACT.]

THIS specification was prepared by a technical committee of the Federal Specifications Board in coöperation with the Soap Committee of the Soap Section of the American Specialty Manufacturers' Association, and was promulgated by the Federal Specifications Board on June 20, 1922. The specification gives the general requirements and detailed methods of sampling and testing, the preparation of the reagents required, and the basis of purchase. The methods of sampling and testing were prepared by a committee of the American Chemical Society in coöperation with the two committees mentioned above. The general requirements are:

The soap desired under this specification is a soap well made from pure coconut oil and the necessary alkali. It must be entirely soluble in both sea water and fresh water, and make a suitable lather. Bidder shall state size, weight and number of cakes in each box.

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[10] Circular No. 126.

Failure to meet any of the following requirements will be cause for rejection:

Matter volatile at 105° C. shall not exceed 55 per cent.

Deliveries which yield more than 55 per cent. of volatile matter will be rejected without further test.

Total matter insoluble in alcohol shall be not less than 2 per cent. nor more than 3 per cent., and shall consist essentially of sodium carbonate (Na_2CO_3).

Free alkali, calculated as sodium hydroxide ($NaOH$) shall not exceed 0.5 per cent.

Matter insoluble in water shall not exceed 0.5 per cent.

Chloride, calculated as sodium chloride ($NaCl$), shall be not less than 2.5 per cent. nor more than 3.5 per cent.

Rosin, sugar and foreign matter shall not be present.

The acid number of the mixed fatty acids prepared from the soap shall be not less than 250.

The percentage of matter volatile at 105° C. will be computed on the basis of the soap as received, but all other constituents will be calculated on the basis of material containing 55 per cent. of volatile matter. The material will be purchased by net weight.

UNITED STATES GOVERNMENT SPECIFICATION FOR AUTOMOBILE SOAP.[11]

[ABSTRACT.]

THIS specification was prepared by a technical committee of the Federal Specifications Board in coöperation with the Soap Committee of the Soap Section of the American Specialty Manufacturers' Association, and was promulgated by the Federal Specifications Board on June 20, 1922. The specification gives the general requirements and detailed methods of sampling and testing, the preparation of the reagents required, and the basis of purchase. The methods of sampling and testing were prepared by a committee of the American Chemical Society in coöperation with the two committees mentioned above. The general requirements are:

The soap desired under this specification is a pure vegetable-oil paste soap, containing no free alkali or acid; relatively free from matter insoluble in alcohol; homogeneous; free from adulterants of any kind and without objectionable odor. Bidder to state size and weight of unit.

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[11] Circular No. 127.

Failure to meet any of the following requirements will be cause for rejection:

Matter volatile at 105° C. shall not exceed 55 per cent. Deliveries which yield more than 55 per cent. of volatile matter will be rejected without further test.

The sum of free alkali and total matter insoluble in alcohol shall not exceed 1.0 per cent.

Free alkali, calculated as sodium hydroxide (NaOH), shall not exceed 0.2 per cent.

Free acid, calculated as oleic, shall not exceed 0.2 per cent.

Matter insoluble in water shall not exceed 0.2 per cent.

Unsaponified matter shall not exceed 4.0 per cent.

Rosin shall not be present.

Odor must be as specified in contract.

The percentage of matter volatile at 105° C. will be computed on the basis of the soap as received, but all other constituents will be calculated on the basis of material containing 50 per cent. of volatile matter.

The material will be purchased by net weight.

UNITED STATES GOVERNMENT SPECIFICATION FOR CHIP SOAP.[12]

[ABSTRACT.]

THIS specification was prepared by a technical committee of the Federal Specifications Board in coöperation with the Soap Committee of the Soap Section of the American Specialty Manufacturers' Association, and was promulgated by the Federal Specifications Board on June 20, 1922. The specification gives the general requirements and detailed methods of sampling and testing, the preparation of the reagents required, and the basis of purchase. The methods of sampling and testing were prepared by a committee of the American Chemical Society in coöperation with the two committees mentioned above. The general requirements are:

The soap desired under this specification is a soap in chip form, made from soda and fats, without rosin, as free as possible from water and all substances other than true soap, of a light uniform color, free from disagreeable odor, and suitable for high-grade laundry work with soft water, when the presence of alkaline salts is objectionable.

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[12] Circular No. 128.

Bidder shall state size and weight of package.

Failure to meet any of the following requirements will be cause for rejection:

Matter volatile at 105° C. shall not exceed 15 per cent. Deliveries which yield more than 15 per cent. of volatile matter will be rejected without further test.

The sum of free alkali, total matter insoluble in alcohol and sodium chloride shall not exceed 3.0 per cent.

Free alkali, calculated as sodium hydroxide ($NaOH$) shall not exceed 0.5 per cent.

Matter insoluble in water shall not exceed 0.2 per cent.

Titer of the mixed fatty acids prepared from the soap must be not less than 39° C.

Color and odor must be as specified.

The percentage of matter volatile at 105° C. will be computed on the basis of the soap as received, but all other constituents will be calculated on the basis of material containing 10 per cent. of volatile matter.

The material will be purchased by net weight, provided the matter volatile at 105° C. does not exceed 10 per cent. With deliveries containing more than 10 per cent., but not exceeding 15 per cent. of matter volatile at 105° C., settlement will be made on the basis of 10 per cent. of matter volatile at 105° C., *i.e.,* nine-tenths (9-10) of a pound of non-volatile matter will be considered one (1) pound of soap.

UNITED STATES GOVERNMENT SPECIFICATION FOR ORDINARY LAUNDRY SOAP.[13]

[ABSTRACT.]

This specification was prepared by a technical committee of the Federal Specifications Board in coöperation with the Soap Committee of the Soap Section of the American Specialty Manufacturers' Association, and was promulgated by the Federal Specifications Board on June 20, 1922. The specification gives the general requirements and detailed methods of sampling and testing, the preparation of the reagents required, and the basis of purchase. The methods of sampling and testing were prepared by a committee of the American Chemical Society in coöperation with the two committees mentioned above. The general requirements are:

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[13] Circular No. 129.

The soap desired under this specification is a well made, uniformly mixed laundry or common soap, made from soda and fats, with no excessive proportion of rosin and a moderate amount of matter insoluble in alcohol; free from objectionable odor or makeweights; suitable for use with moderately hard water for general cleaning and laundry purposes.

Bidder shall state size, weight and number of cakes in each box.

Failure to meet the following requirements will be cause for rejection:

Matter volatile at 105° C. shall not exceed 36 per cent. Deliveries which yield more than 36 per cent. volatile matter will be rejected without further test.

The sum of free alkali, total matter insoluble in alcohol and sodium chloride shall be not less than 2 per cent. nor more than 10 per cent.

Free alkali calculated as sodium hydroxide ($NaOH$) shall not exceed 0.5 per cent.

Matter insoluble in water shall not exceed 1.0 per cent.

Rosin shall not exceed 25 per cent.

The percentage of matter volatile at 105° C. will be computed on the basis of the soap as received, but all other constituents will be calculated on the basis of material containing 34 per cent. of volatile matter.

The material will be purchased by net weight provided the matter volatile at 105° C. does not exceed 34 per cent. With deliveries containing more than 34 per cent. but not exceeding 36 per cent. of matter volatile at 105° C., settlement will be made on the basis of 34 per cent. of matter volatile at 105° C., *i.e.*, sixty-six one-hundredths (66-100) of a pound of non-volatile matter shall be considered one (1) pound of soap.

UNITED STATES GOVERNMENT SPECIFICATION FOR GRIT CAKE SOAP.[14]

[ABSTRACT.]

THIS specification was prepared by a technical committee of the Federal Specifications Board in coöperation with the Soap

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[14] Circular No. 130.

Committee of the Soap Section of the American Specialty Manufacturers' Association, and was promulgated by the Federal Specifications Board on June 20, 1922. The specification gives the general requirements and detailed methods of sampling and testing, the preparation of the reagents required, and the basis of purchase. The methods of sampling and testing were prepared by a committee of the American Chemical Society in coöperation with the two committees mentioned above. The general requirements are:

(*a*) *Grit Cake Soap, for Fine Work, Such as Glass and Enamel.*—The material desired under this specification is a compact cake soap containing about nine-tenths of its weight of clean, finely divided, siliceous material, which will not scratch glass or enameled surfaces, unscented and of a light gray or white color. Cakes to be well compressed and of a satisfactory degree of friability which must not be materially affected or lessened after immersion in, or contact with, water. Bidder shall state size, weight and number of cakes to each box.

Failure to meet any of the following requirements will be cause for rejection:

Matter volatile at 105° C. shall not exceed 4 per cent. Deliveries which yield more than 4 per cent. of volatile matter shall be rejected without further test.

Alkali is alkaline salts (total alkalinity of matter insoluble in alcohol) calculated as sodium carbonate (Na_2CO_3) shall not exceed 1.0 per cent.

Free alkali calculated as sodium hydroxide ($NaOH$) shall not exceed 0.1 per cent.

Insoluble siliceous material shall be not less than 88 per cent. nor more than 93 per cent. This insoluble siliceous material must be mainly ground feldspar and all must pass a No. 100 screen and at least 95 per cent. must pass a No. 200 screen.

Rosin, sugar and foreign matter shall not be present.

Anhydrous soda soap shall be within 1 per cent. of the difference between 100 and the sum of the matter volatile at 105° C. insoluble siliceous material and alkali as alkaline salts.

Material will be purchased by net weight.

(*b*) *Grit Cake Soap; For Scouring and Scrubbing.*—The material desired under this specification is a compact cake soap containing about four-fifths of its weight of clean, finely divided, siliceous material; unscented and of a light gray or white color. Cakes to be well compressed and of a satisfactory degree of friability which must not be materially affected or lessened after immersion in, or contact with, water. Bidder shall state size, weight and number of cakes to the box.

Failure to meet any of the following requirements will be cause for rejection:

Matter volatile at 105° C. shall not exceed 5 per cent. Deliveries which yield more than 5 per cent. of volatile matter shall be rejected without further test.

Alkali as alkaline salts (total alkalinity of matter insoluble in alcohol) calculated as sodium carbonate (Na_2CO_3) shall not exceed 3 per cent.

Free alkali calculated as sodium hydroxide ($NaOH$) shall not exceed 0.1 per cent.

Insoluble siliceous material shall be not less than 75 per cent. nor more than 85 per cent. This insoluble siliceous material should be mainly quartz. It all must pass a No. 100 screen.

Rosin, sugar and foreign matter shall not be present.

Anhydrous soda soap shall be within 1 per cent. of the difference between 100 and the sum of the matter volatile at 105° C., insoluble siliceous material and alkali as alkaline salts.

Material will be purchased by net weight.

UNITED STATES GOVERNMENT SPECIFICATION FOR SCOURING COMPOUNDS, FOR FLOORS, (*a*) AND (*b*) AND SOAP SCOURING COMPOUND (*c*).[15]

[ABSTRACT.]

This specification was prepared by a technical committee of the Federal Specifications Board in coöperation with the Soap Committee of the Soap Section of the American Specialty Manufacturers' Association, and was promulgated by the Federal Specifications Board on June 20, 1922. The specification gives the general requirements and detailed methods of sampling and testing, the preparation of the reagents required, and the basis of purchase. The methods of sampling and testing were prepared by a committee of the American Chemical Society in coöperation with the two committees mentioned above. The general requirements are:

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[15] Circular No. 131.

(*a*) *Scouring Compound for Fine Marble Floors.*—The material desired under this specification is a uniform powder containing about nine-tenths of its weight of clean, finely divided, siliceous material, the remainder being sodium carbonate, or soap or both. It must not scratch nor discolor the surfaces on which it is to be used; to be unscented and of a light gray or white color. Bidder shall state size and weight of package.

Failure to meet any of the following requirements will be cause for rejection:

Matter volatile at 105° C. shall not exceed 10 per cent.

The sum of sodium carbonate and anhydrous soap shall not exceed 7 per cent. nor be less than 2 per cent.

Free alkali calculated as sodium hydroxide ($NaOH$) shall not exceed 0.1 per cent.

Insoluble siliceous material shall be not less than 85 per cent. nor more than 95 per cent. It all must pass a No. 100 screen and at least 95 per cent. must pass a No. 200 screen; it must not scratch marble.

Material will be purchased by net weight.

(*b*) *Scouring Compound for Tile or Ceramic and Terrazzo Floors.*—The material desired under this specification is a uniform powder containing about nine-tenths of its weight of clean, finely divided siliceous material, the remainder being sodium carbonate or soap, or both; to be unscented and of a light gray or white color. Bidder shall state size and weight of package.

Failure to meet any of the following requirements will be cause for rejection:

Matter volatile at 105° C. shall not exceed 10 per cent.

The sum of sodium carbonate (Na_2CO_3) and anhydrous soap shall not exceed 10 per cent. nor be less than 2 per cent.

Insoluble siliceous material shall be not less than 85 per cent. nor more than 95 per cent. Ninety per cent. must pass a No. 80 screen and at least 99 per cent. must pass a No. 60 screen.

Free alkali calculated as sodium hydroxide ($NaOH$) shall not exceed 0.1 per cent.

Material will be purchased by net weight.

(*c*) *Soap Scouring Compound.*—The material desired under this specification is a mixture of finely powdered, light colored siliceous material, sodium carbonate, and powdered soap; it must be free from caustic alkali and be unscented. Bidder shall state size and weight of package.

Failure to meet any of the following requirements will be cause for rejection:

Matter volatile at 105° C. shall not exceed 10 per cent.

Carbonated alkali calculated as sodium carbonate (Na_2CO_3) shall be not less than 15 per cent. nor more than 20 per cent.

Free alkali calculated as sodium hydroxide ($NaOH$) shall not exceed 0.1 per cent.

Anhydrous soap shall be not less than 5 per cent. nor more than 10 per cent.

Insoluble siliceous material shall be not less than 60 per cent. nor more than 80 per cent. Ninety per cent. must pass a No. 80 screen and at least 99 per cent. shall pass a No. 60 screen.

UNITED STATES GOVERNMENT SPECIFICATION FOR HAND GRIT SOAP.[16]

[abstract.]

This specification was prepared by a technical committee of the Federal Specifications Board in coöperation with the Soap Committee of the Soap Section of the American Specialty Manufacturers' Association, and was promulgated by the Federal Specifications Board on June 20, 1922. The specification gives the general requirements and detailed methods of sampling and testing, the preparation of the reagents required, and the basis of purchase. The methods of sampling and testing were prepared by a committee of the American Chemical Society in coöperation with the two committees mentioned above. The general requirements are:

The material desired under this specification is a high-grade cake soap containing about one-third its weight of clean, finely divided, insoluble, siliceous matter; as free as possible from water; either uncolored or colored in a manner indicated in the contract; either unscented or perfumed in a manner indicated in the contract of the same; thoroughly saponified; well compressed in firm, smooth cakes.

Bidder shall state size, weight and number of cakes in each box.

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[16] Circular No. 132.

Failure to meet any of the following requirements will be cause for rejection:

Matter volatile at 105° C. shall not exceed 25 per cent. Deliveries which yield more than 25 per cent. of volatile matter will be rejected without further test.

Alkali as alkaline salts (total alkalinity of matter insoluble in alcohol) calculated as sodium carbonate (Na_2CO_3) shall not exceed 1.0 per cent.

Free alkali calculated as sodium hydroxide ($NaOH$) shall not exceed 0.1 per cent.

Insoluble siliceous material shall be not less than 25 nor more than 40 per cent. This siliceous material must be so finely ground that not less than 98 per cent. of it will pass through a No. 100 screen and not less than 90 per cent. of it will pass through a No. 200 screen.

Rosin, sugar and foreign matter shall not be present.

Anhydrous soda soap shall be within 1 per cent. of the difference between 100 and the sum of matter volatile at 105° C., insoluble siliceous material and alkali as alkaline salts.

The percentage of matter volatile at 105° C. will be computed on the basis of the soap as received, but all other constituents will be calculated to the basis of material containing 25 per cent. of matter volatile at 105° C.

Material will be purchased by net weight.

Qualitative Test for Uranium.—HAROLD D. BUELL, of Syracuse University (*Jour. Ind. Eng. Chem.*, 1922, xiv, 593), has devised the following qualitative test for uranium. A solution of the sample in nitric acid is prepared. An excess of granulated zinc is added, and the reaction is permitted to continue until the acid is spent. If the reaction occur too slowly, more nitric acid is added; if too violently, the solution is diluted with water. A yellow deposit forms on the excess (undissolved) zinc if uranium be present. This deposit apparently has the formula $UO_2.2H_2O$. This test may not be applied in the presence of sulphuric acid or hydrochloric acid. Gold, platinum, tungsten, lead, mercury, copper, titanium, chromium, and thorium do not interfere with the test. Iron and vanadium interfere only when present in large amounts; in such a case, the spent liquid is removed; the excess zinc and the precipitate are treated with sufficient nitric acid to start a reaction; the precipitate dissolves; and the yellow deposit appears as the acid is exhausted. This test is sufficiently sensitive to show the presence of 0.88 millegram of uranium in 1 cubic centimetre of solution. J. S. H.

NOTES FROM THE RESEARCH LABORATORY EASTMAN KODAK COMPANY.*

ELECTROCHEMICAL ASPECTS OF PHOTOGRAPHIC DEVELOPMENT.[1]

By S. E. Sheppard.

[ABSTRACT.]

THE early part of this paper discusses the history of the theory of development as a reversible chemical reaction. The conception of reduction potentials is considered, and it is pointed out that two different methods of presentation have been evolved. According to one reduction potential depends on the transfer of electric charges while according to the other it depends on the decomposition of water and release of atomic hydrogen. It is shown that under certain conditions these two conceptions are equivalent to each other in determining true reduction potentials. The principle condition is the presence in equilibrium of the reduction and oxidation products of the reaction. The work of F. C. Frary and A. H. Nietz is considered in this connection. Before satisfactory reduction potentials for organic developing reagents can be determined the following data must be secured:

A. Determination of the state in solution of the reducing agents;

B. Nature, and to some extent, the velocities of the reaction;

C. Silver equivalent of the reducer during the working period of development.

As contributory to these points the ionization constants of paraminophenol, elon, hydroquinone, and pyrogallol have been determined from the electrometric titration curves.

THE REMOVAL OF FREE ACID FROM NITROCELLULOSE WITH SPECIAL REFERENCE TO THE USE OF SALINE LEACHES.[2]

By S. E. Sheppard.

[ABSTRACT.]

THIS paper contains an account of the physical chemistry of the removal of acid from nitrocotton. Evidence is brought

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* Communicated by the Director.

[1] Communication No. 121 from the Research Laboratory of the Eastman Kodak Company and published in *Trans. Amer. Electrochem. Soc.*, 1921, p. 29.

[2] Communication No. 128 from the Research Laboratory of the Eastman Kodak Company and published in *J. Ind. Eng. Chem.*, 699, 1921.

forward that the last traces in the order of 1 per cent. of acid retained by nitrocellulose is not held mechanically but adsorbed, the evidence in favor of this being mainly the effect of heat and of saline leaches, respectively, in accelerating the removal of the acid and changing the course of the curve expressing the rate of removal. The use of concentrated saline leaches, notably that of sodium sulphate, is discussed in detail and its application to the purification of nitrocellulose. From special experiments on the combination of pulping with other treatment it is concluded that the effect of pulping is mainly valuable on a large scale in procuring uniformity and of little direct effect on the fibres. From experiments on partial reprecipitation of nitrocellulose from acetone solutions and centrifugal fractionation, it is considered " stabilizing treatments " are less concerned with the chemical destruction of cellulose sulfuric esters and of lower nitrates of cellulose than with peptization and removal of cellulose dextrin derivatives.

THE ACTION OF SOLUBLE IODIDES AND CYANIDES ON THE PHOTOGRAPHIC EMULSION.[3]

By S. E. Sheppard.

[ABSTRACT.]

A RE-EXAMINATION of the fogging action of iodides on photographic emulsions discussed by Sheppard and Meyer in the *Photographic Journal* (60, 12, 1920) has been made. In a subsequent paper Mr. F. F. Renwick reported the discovery of a red sensitizing action of soluble iodides and cyanides on the emulsion, and attributed the fogging action observed by Sheppard and Meyer to such a sensitizing effect. In the present paper it is shown that with the emulsions used by Sheppard and Meyer bathing with potassium iodide produces practically no red sensitizing, but that this is effected with the emulsions used by Renwick. An investigation of a large number of commercial emulsions showed the effect to be specific to certain emulsions. In discussing the mechanism of such red sensitizing by iodides and cyanides evidence is brought forward contrary to Renwick's hypothesis and favoring a photocatalytic explanation; it is suggested that the orienting effect of the iodine ion of the silver halide crystal lattice modifies the aggregation of colloid silver produced by light of short wave-lengths so that sensitizing for longer wave-lengths is effected.

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[3] Communication No. 130 from the Research Laboratory of the Eastman Kodak Company and published in *Photo. J.*, **88**, 1922.

NOTES FROM THE U. S. BUREAU OF CHEMISTRY.*

A STUDY OF METHODS OF MINIMIZING SHRINKAGE IN SHELL EGGS DURING STORAGE.[1]

By L. H. Almy, H. I. Macomber, and J. S. Hepburn.

[ABSTRACT.]

IMMERSION of eggs for short periods in heated or unheated solutions of mineral or organic acids, mineral salts, or soap in water were of but slight value in reducing shrinkage in eggs held at room or higher temperature. The loss in weight of eggs treated with heated cotton-seed oil was 6.3 per cent. and that of those treated with a heated mineral oil (specific gravity 0.869, flash point 350° F., viscosity at 100° F. 134 units, Saybolt) was 7.4 per cent. of that of untreated eggs. Lighter mineral oils, two other vegetable oils, and an animal oil were less satisfactory. Addition of gums, waxes, or rosin failed to increase the efficiency of the better mineral oil. The presence of 1 or 2 per cent. of soap markedly increased the sealing value of the more inferior mineral oils.

THE ROLE OF CYSTINE IN THE DIETARY PROPERTIES OF THE PROTEINS OF THE COW-PEA, VIGNA SINENSIS, AND OF THE FIELD PEA, PISUM SATIVUM.[2]

By A. J. Finks, Carl O. Johns, and D. Breese Jones.

[ABSTRACT.]

THE proteins of the cow-pea, *Vigna sinensis,* like those of the *Phaseolus* beans, are limited in their nutritive value by a deficiency of cystine and by an indigestibility which can be remedied by cooking. Only one-third to two-thirds of the normal rate of growth of albino rats was obtained on a diet in which 70 per cent. of cow-pea meal, equivalent to 16.5 per cent. of protein, furnished the sole source of protein.

Field-pea (*Pisum sativum*) meal, fed at the same protein level,

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* Communicated by the Chief of the Bureau.

[1] Published in *J. Ind. Eng. Chem.,* 14 (1922) : 525.

[2] Published in *J. Biol. Chem.,* 52 (1922) : 403.

enabled rats to grow at a practically normal rate without the addition of cystine and without cooking.

The proteins of the field pea and those of the cooked cow-pea plus cystine were equally efficient in promoting growth at a practically normal rate, while the proteins of the cow-pea, raw plus cystine, or cooked without cystine, were less than half as well utilized as those of the field pea.

SAUERKRAUT AND ITS PRODUCTION.[3]

By Edwin LeFevre.

[ABSTRACT.]

CABBAGE is properly cured by the acid brine formed by the action of a group of lactic bacteria always present on cabbage. The presence of yeasts is not essential to this fermentation. A temperature of approximately 86° F. is required to secure the maximum activity of the fermenting organisms. If properly fermented under sanitary conditions sauerkraut, fermented salt cabbage, is a pure and wholesome product. The best way to market it is in the canned form.

WOOL SCOURING WASTES FOR FERTILIZER PURPOSES.[4]

By F. P. Veitch.

[ABSTRACT.]

MORE than 600,000,000 pounds of wool are scoured in this country annually. On the average, the grease content of this wool is approximately 14 per cent. and the potash (K_2O) content is about 4 per cent., while nitrogenous constituents other than those of the wool itself fall below 1 per cent., on the basis of the unscoured wool. The possibility of utilizing the potash and nitrogenous constituents for fertilizer purposes is being studied in the Bureau of Chemistry. Experiments on the manufacturing scale have shown that the material can be handled satisfactorily in the factory. The problem which remains to be solved is, whether or not these materials can be recovered and used economically.

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[3] Published in *Canner*, Vol. 55, No. 2, Serial No. 1432, p. 27.

[4] Published in *J. Ind. Eng. Chem.*, 14 (1922): 434.

NOTES FROM THE U. S. BUREAU OF MINES.*

APPLICATION OF THE GEOPHONE TO MINING.

By Alan Leighton.

THE geophone, which was invented by the French during the World War to detect underground mining operations, was developed by the United States Engineers, and the instruments now used by the Bureau of Mines were made according to plans drawn by the Engineers, except for the introduction of different diaphragms.

By the use of two geophones, one instrument to each ear, it is possible to determine the direction from which a sound is coming through the earth. A perpendicular, erected halfway between the instruments, according to principles worked out by the Bureau's investigators, will give the direction of the source of sound, or, more accurately, the projection of this line of direction on the horizontal plane will pass through the source of sound.

For use in determining the best ways of operating the geophone for rescue work in mine accidents, and for mine surveying, data must show two things: (1) The proper place to locate the geophone, and (2) the proper place to pound, in order that sounds may be detected and their point of origin determined. Rails and pipe lines can not be relied on to transmit the sounds from blows of different sorts, unless these lines are properly suspended throughout their length. Clay veins or faults interfere greatly with attempts to ascertain the direction from which the sound is coming.

Observations made over the Bureau's experimental mine through the greatest depth of cover—138 feet—show that pounding on the rib with either a timber or a sledge can be perceived on the surface anywhere within a circle whose diameter is 700 to 800 feet, the pounding being located at the centre of this circle. The experiments showed that a blow struck in a mine, with the purpose of being detected by the geophone, should be struck upon the coal. To detect sounds coming through the strata, the instrument should be placed on a niche or shelf of coal rather than on the floor of the mine. An entombed miner should keep up a continuous, though not rapid, pounding, if geophones are used in rescue work at that mine.

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* Communicated by the Director.

Geophones supply a quick and fairly accurate method of mine surveying. They can be used to advantage in guiding tunnels together, in preventing accidents at blasting through, and in locating mine fires, bore holes, faults, and "clay veins." The complete report on the geophone with illustrations has just appeared as Bureau of Mines Technical Paper No. 277.

COMMINUTED SMOKELESS POWDER FOR BLASTING.

By C. E. Munroe and Spencer P. Howell.

The Bureau of Mines has issued a fourth report of a series of investigations made to ascertain how military explosives can be most efficiently and safely used for industrial blasting. This report describes the physical and chemical properties of comminuted (finely ground) smokeless powder, gives precautions for handling and packing it, and for preparing cartridges and bore-holes in its use, presents in detail the results of field tests in blasting stumps, boulders, and ditches, and compares these results with those obtained from dynamite and other explosives.

As the gaseous products of detonation include poisonous and inflammable carbon monoxide, comminuted smokeless powder is unsuitable for use as an explosive in dusty and gaseous coal mines or in other places where inflammable dust, gases, or vapors may be encountered. Nor should it be used in mines, tunnels, or other close places, unless the ventilation is very good and workmen are not in contact with the poisonous gases produced by it. Comminuted smokeless powder is ignited easily and burns, but is detonated most effectively not by a fuse, but by a No. 6 electric detonator. This powder proved to be sensitive both to percussion and friction; it is much less sensitive to percussion than 40 per cent. straight dynamite, is more sensitive than dry picric acid, and about as sensitive as nitroglycerin and gelatin dynamites. As to propulsive capacity, comminuted smokeless powder rated highest of explosives tested, except dry picric acid. The rate of detonation—which is the measure of its shattering power—was about six per cent. lower than the standard used, though it was the lowest for the explosives tested.

The full report (Serial No. 2386) on comminuted smokeless powder and its usefulness as a blasting agent may be obtained from the Director, U. S. Bureau of Mines.

TELLURIUM.

By H. A. Doerner.

From its chemical nature, tellurium is now known to be a non-metallic element belonging to the sulphur-oxygen group. It is most popularly known through its occurrence in certain gold ores—tellurides—which have been extensively mined in the Cripple Creek mining district, Colorado.

Tellurium is a silver-white solid with metallic lustre, the crystalline form being very brittle and easily powdered. It has a specific gravity of 6.27, melts at 452° C. and boils at red heat, giving off a golden-yellow vapor when air is excluded. When heated in air, tellurium burns with a blue flame tinged with green, and evolves white vapors of tellurium dioxide An amorphous form of tellurium, obtained by reduction and precipitation from solution, has a specific gravity of 6.015, and when heated is changed to the crystalline variety. Tellurium is insoluble in water, carbon disulphide or hydrochloric acids, but it is dissolved by nitric acid or concentrated sulphuric acid. It does not tarnish in moist air, is resistant to alkaline solutions, except concentrated KOH, but it is dissolved by fused alkalies. Its atomic weight has been the subject of much controversy, but the value 127.5 has been generally accepted. The chemistry of tellurium is similar to that of sulphur. It forms three oxides: TeO, TeO_2, and TeO_3; also tellurides, tellurites, and tellurates. A number of halide compounds, a sulphide, and a sulphate are known.

The Bureau of Mines has compiled a brief report (Serial No. 2385) containing a summary of the known facts regarding tellurium, and reference to the published sources of information on the element.

FAILURE OF CENTRE SHOTS IN BLASTING.

By L. C. Ilsley, Electrical Engineer, and A. B. Hooker, Assistant Electrical Engineer.

In blasting on a large scale with a blasting machine, trouble has been experienced with missed shots. The shots that fail to fire are often a group in the centre of the series The Bureau of Mines has conducted field and laboratory tests to ascertain the cause and remedy of the difficulty. The results of the tests showed that if a large number of the common electric detonators are connected in series and fired where the earth is wet, a large leakage of firing current occurs, and the detonators at each end of the series circuit may fire, whereas the middle ones misfire. The detonators near the positive end fire because too little leakage has occurred to cause a misfire; those near the negative end will fire because enough current has returned to the circuit. The middle detonators misfire because the current is not sufficient to fire them before the firing of the end detonators has opened the circuit. The writers make recommendations as to the elimination of the misfiring of the centre shots. This report has been issued by the Bureau of Mines as Serial No. 2384, Reports of Investigations, which is available for distribution.

A Continuous Spectrum from Mercury Vapor. C. D. CHILD. (*Astrophys. J.*, May, 1922.)—From 1890 onward it has been known that mercury vapor can be made to emit a continuous spectrum. The conditions for such an effect are now described for the first time. They are three in number. The current density must be small, the temperature of the vapor must be above 120° C. and below a higher temperature depending on the density of the vapor, and, lastly, the vapor must have a density about the same as that of saturated vapor at 120° C. The best source of current for getting the continuous spectrum is a Wimshurst or Toepler-Holtz machine.

The metallic vapor that gives the continuous spectrum is not just the same as mercury vapor at room temperature, for it emits visible radiation without being ionized and, besides this, it has a lower ionizing potential.

" The carriers of the continuous spectrum are molecules of mercury while the atoms are the carriers of the line spectrum " is the opinion of the author. G. F. S.

From Zurich comes the announcement of the discovery of a new radioactive body. Piccard and Stahel have isolated it and given it the preliminary name UV. It takes 48 days to complete its half change into something else. It belongs in the actinium series. (*Physikal. Zeit.*, Jan. 1, 1922.) Four months later Otto Hahn publishes the results of his investigations, which he interprets as making the existence of UV impossible. No doubt the two Swiss savants will now proceed to do their utmost to establish the existence of their intellectual progeny, and the conflict of evidence will continue until the truth is known and recognized. G. F. S.

THE FRANKLIN INSTITUTE.

MEMBERSHIP NOTES.

CHANGES OF ADDRESS.

Mr. Calvin Barwis, care Interior Oil and Gas Corporation, 302 East Street, Warren, Pennsylvania.

Miss Caroline D. Blackburn, 510 Midvale Avenue, Germantown, Philadelphia, Pennsylvania.

Mr. Edwin Frank, 5227 Wissahickon Avenue, Germantown, Philadelphia, Pennsylvania.

Prof. E. A. Hersam, Massachusetts Institute of Technology, Cambridge 39, Massachusetts.

Mr. Walter C. Hess, 4635 Walnut Street, Philadelphia, Pennsylvania.

Mr. John W. Hornsey, "The Oakes," Norton, N. Sheffield, England.

Mr. Isaac W. Jeanes, Room 908, Lafayette Building, Philadelphia, Pennsylvania.

Mr. James A. Wright, 141 Stanley Street, Montreal, Quebec, Canada.

NECROLOGY.

Mr. Coleman Sellers, Jr., 1600 Hamilton Street, Philadelphia, Pennsylvania.

Mr. David H. Wilson, Jr., 253 Thirty-sixth Street, Brooklyn, New York.

Lieut. A. B. Wyckoff, Ontario, California.

LIBRARY NOTES.

PURCHASES.

American Concrete Institute.—Proceedings 1922.

Day, David T. [ed.].—Handbook of the Petroleum Industry. 2 vols. 1922.

Martineau, George.—Sugar, Cane and Beet. An Object Lesson. No date.

Who's Who in America. 1922–1923.

Who's Who in Engineering. 1922–1923.

GIFTS.

American Car and Foundry Company, Twenty-third Annual Report for Year Ending April 30, 1922. Jersey City, New Jersey, 1922. (From the Company.)

Baker, Joseph, Sons and Perkins Company, Incorporated, Catalogue No. 3 of Universal Mixing and Kneading Machines. White Plains, New York, 1922. (From the Company.)

Catholic University of America, Year-book 1922–1923. Washington, District of Columbia, 1922. (From the University.)

Clark University, Catalogue 1922–1923. Worcester, Massachusetts, 1922. (From the University.)

Cleveland, Cincinnati, Chicago and St. Louis Railway Company, Thirty-third Annual Report of the Board of Directors to the Stockholders for the Year Ended December, 1921. Cincinnati, Ohio, 1922. (From the Company.)

Colorado Scientific Society, Year-book 1882–1919 and Reprints from Proceedings of the Society, June, 1919, and January, 1922. Denver, Colorado. (From the Society.)

Columbia University, Announcement, School of Business, 1922–1923. New York City, New York, 1922. (From the University.)

Copper and Brass Research Association, Copper Roofing Information for Architects and Roofing Contractors. New York City, New York, 1922. (From the Association.)

Crosby Valve and Engineering Company, Limited, How to Control Cupola Blast. London, England, 1922. (From the Company.)

Dover Boiler Works, Catalogue No. 30. Dover, New Jersey, 1922. (From the Works.)

Electric Furnace Construction Company, Electric Furnaces, Electro Steam Boilers. Philadelphia, Pennsylvania, 1922. (From the Company.)

English Electric Company, Limited. Pamphlets 357 and 359 of Electric Locomotives. London, England, 1922. (From the Company.)

General Electric Company, Bulletin of Air Compressor Governors and General Electric Catalogue for 1921. Schenectady, New York, 1922. (From the Company.)

Ham, Baker and Company, Sluice Valves. London, England, 1922. (From the Company.)

Hupp Motor Car Corporation, Hupmobile Construction Details. Detroit, Michigan, 1922. (From the Corporation.)

India Geological Survey, Memoirs, Vol. 48. Calcutta, India, 1922. (From the Survey.)

Indiana University, Catalogue for 1922. Bloomington, Indiana, 1922. (From the University.)

Institut Geologico de Espana, Memorias, Tomo IV. Madrid, Spain, 1922. (From the Institute.)

Institute of Metals, Journal, Vol. 27, No. 1. London, England, 1922. (From the Institute.)

Institution of Civil Engineers, Minutes of Proceedings, Vol. 212. London, England, 1921. (From the Institution.)

Iowa Railroad Commissioners, Forty-fourth Annual Report for Year Ending December 5, 1921. Des Moines, Iowa, 1922. (From the Commissioners.)

Jacobs Manufacturing Company, Jacobs Chucks. Hartford, Connecticut, 1922. (From the Company.)

Johnson and Phillips, Limited, Transformer Abstracts, 1 to 10. London, England, 1922. (From the Company.)

Leather Belting Exchange, Specifications for Leather Belting. Washington, District of Columbia, 1922. (From the Exchange.)

Lowell Textile School, Bulletin of the School, May, 1922. Boston, Massachusetts, 1922. (From the School.)

Osterhout Free Library, Thirty-third Annual Report for 1921. Wilkes-Barre, Pennsylvania, 1921. (From the Library.)

Pan-American Petroleum and Transport Company, Mexican Petroleum. New York City, New York, 1922. (From the Company.)

Parkesburg Iron Company, Application and Maintenance of Charcoal Iron Boiler Tubes. Parkesburg, Pennsylvania, 1922. (From the Company.)

Pennsylvania Department of Labor and Industry, Annual Report Bureau of Employment, 1921. Harrisburg, Pennsylvania, 1922 (From the Department.)

Philadelphia Board of Directors of City Trusts, Fifty-second Annual Report, 1921. Philadelphia, Pennsylvania, 1921. (From the Directors.)

Philadelphia City Council, Manual for 1922. Philadelphia, Pennsylvania, 1922. (From President of City Council.)

Pittsburgh, Cincinnati, Chicago and St. Louis Railroad Company, Fifth Annual Report, for Year Ended December, 1921. Pittsburgh, Pennsylvania, 1922. (From the Secretary.)

Providence City Engineer, Annual Report of the Engineer for 1921. Providence, Rhode Island, 1922. (From the City Engineer.)

Robins Conveying Belt Company, Handbook of Conveyor Practice. Philadelphia, Pennsylvania, 1922. (From the Company.)

Rogers and Hubbard Company, How to Case-Harden, Color and Anneal with Granulated Raw Bone. Middletown, Connecticut, no date. (From the Company.)

Rugby Engineering Society, Proceedings, Vol. 14, Session 1919–20. Rugby, England, 1921. (From the Society.)

Ruston and Hornsby, Limited, The Triumph of Oil Fuel. Lincoln, England, 1922. (From the Company.)

Sellers, William, and Company, Incorporated, Locomotive Injectors and Boiler Attachments. Philadelphia, Pennsylvania, 1922. (From the Company.)

Service Geographique de l'Armee Hellenique, Comptes Rendus de Service, 1921. Athens, Greece, 1922. (From the Commandant.)

Smithsonian Institution, Annual Report for 1920. Washington, District of Columbia, 1922. (From the Institution.)

Southern Pacific Company, Thirty-eighth Annual Report for Year Ended December 31, 1921. New York City, New York, 1921. (From the Company.)

Southern Railway System, A Record of Growth, 1911–1920 Washington, District of Columbia, 1922. (From the Secretary.)

Stein and Atkinson, Limited, Stein-Chapman Gas Producers and Stein Furnaces. London, England, 1922. (From the Company.)

Trist, Ronald and Company, Limited, Booklet of Sand-blasting. London, England, 1922. (From the Company.)

University of Louisville, Catalogue and Announcements 1922–1923. Louisville, Kentucky, 1922. (From the University.)

University of Minnesota, An Investigation of Secondary Stresses in the Kenova Bridge, by G. A. Maney and John I. Parcel. Minneapolis, Minnesota, 1922. (From the University.)

University of Oklahoma, Catalogue, 1921–22, and Calendar, 1922–23. Norman, Oklahoma, 1922. (From the University.)

University of Tennessee, Register 1921–22 and Announcement 1922–23. Knoxville, Tennessee, 1922. (From the University.)

University of Texas, Catalogue, 1921–22. Austin, Texas, 1921. (From the University.)

Waltham Department of Public Works, Annual Report for 1921. Waltham, Massachusetts, 1922. (From the Department.)

Western Australia Department of Statistics, Statistical Register for 1920–21 and Previous Years. Perth, Australia, 1922. (From the Government Statistician.)

Whiting Corporation, Whiting Railroad Equipment, Catalogue 160. Harvey, Illinois, 1922. (From the Corporation.)

BOOK NOTICES.

DISCOURS ET MÉLANGES. Emile Picard, Permanent Secretary of the Academy of Sciences. 8vo, paper bound, 292 pages. Paris, Gauthier-Villars et Cie. Price, 10 francs, net.

This volume reminds one of Berthelot's "Science et Morale," being a collection of essays and addresses by the author, covering a wide range of subjects. There are biographies, essays on contemporary problems, notes on the history of science, pure and applied. Much of the book, of course, has a local value only, but several articles have a wider interest, among which we note one on the pretensions of Germany to a hegemony in science, another on anti-typhoid vaccination, and a third on the low birth-rate problem. In the last eight years, France has passed through a terrific crisis, and the feeling awakened by that experience must be reflected in its literature. One manifestation of this is the essay on the German claim to leadership in science. We all know of this, and the assertion should be especially galling to France, which, during the latter half of the eighteenth and first half of the nineteenth centuries, enjoyed, in almost all fields of science and philosophy, a leading part. It is, however, an ungracious task to discuss the relative values of the work of the scientists and philosophers of any age and time. As might be expected, Monsieur Picard gives but little acknowledgment to German workers. How far an appreciation of the service that England rendered at such great sacrifice awakens the passing compliments to inventors and discoverers born on the other side of "The Sleeve," cannot be determined, but extravagant claims are made for French work in almost all fields. A curious effort is made to trace the lack of real efficiency in German science to the nature of the language. No thoroughfare can be found in that direction. Each cultivated nation regards its language as the best adapted for the expression of thought, and it is hardly possible that one accustomed from infancy to a particular form can appreciate fully the value of another. English-speaking persons realize the advantage of the absence of distinctions of gender in ordinary nouns, and are much annoyed by the necessity of observing such distinctions in using the Continental tongues, yet those who are brought up in such distinctions consider them useful, although it must be noted that all recent suggestions of an artificial language, such as Volapük, Esperanto and Ido, avoid all distinctions of gender, except those belonging to actual sexes, and also avoid all modifications of the adjective in relation to the noun. Fichte claimed that German was a fundamental language, while

English is a hybrid, but there is no reason to regard his opinion as sound; it has pleased the Germans, and has been repeated by them of late years.

In his essay on the claims of Germany to a hegemony in science, our author is hardly thorough or entirely fair. He endeavors to place French work at the head of every list, an effort that was, of course, pleasing to his audience, and no doubt received with enthusiastic applause.

One of the essays worth special notice is that on aviation in France in 1909. An introduction dealing with the early history of aerial physics is given. Icarus is not mentioned, but Leonardo da Vinci is, and Montgolfier. The history of the development of the heavier-than-air machine is outlined, and while almost all those who have figured in the experimental work are mentioned, no reference is made to Langley. The omission can hardly be accidental, and it shows how narrow and prejudiced the French mind can be. The action is dastardly, and indicates that, however eminent M. Picard may be in the fields in which he labors, he lacks the judicial attitude that is an essential characteristic of science.

HENRY LEFFMANN.

UNITED STATES GEOLOGICAL SURVEY, Professional Paper No. 123, A Superpower System for the Region between Boston and Washington, by W. S. Murray and others. 261 pages, illustrations, plates, maps, quarto. Washington, Government Printing Office, 1921.

There is one very striking point on the title-page. It is the statement: "by W. S. Murray and others." It is common knowledge that important investigations require large staffs, but it is rare to see any one give credit to the "others" in the way that Mr. Murray does, both on the title-page and throughout the report.

The report is preceded by a full table of contents, and followed by a most excellent index, so that it is easily possible to locate any of the valuable information contained.

FOREWORD.

Dr. George Otis Smith, Director of the United States Geological Survey, has written a foreword in which he outlines the developments leading up to the survey and report. He shows how at Mr. Murray's instigation the matter was presented to the Secretary of the Interior and to Congress. This resulted in an appropriation by Congress of $125,000 for the fiscal year 1921 for the following purpose:

> For the survey of power production and distribution in the United States, including the study of methods for the further utilization of water-power, and the special investigation of the possible economy of fuel, labor, and materials resulting from the use in the Boston-Washington industrial region of a comprehensive system for the generation and distribution of electricity to transportation lines and industries, and the preparation of reports thereon.

The language of the act is so clear that it needs no further comment. The work was organized in July, 1920, under Mr. Murray and a special staff of engineers. Regular members of the Department of the Interior also contributed actively to the work.

To supplement the detail work to be done by the engineering staff, an advisory board "consisting of men of vision and experience, representing our railroads, both steam and electric, and manufacturing, engineering and chemical industries," was appointed, which served without compensation.

The report was completed on schedule on June 30, 1921, was printed, and has only recently become available to the public.

SUMMARY REPORT.

Mr. Murray has condensed the report into the small space of sixteen pages. Following this are appendixes dealing with the details of the various sections.

It is not necessary to point out the great place that power has in modern industrial life. Mr. Murray has used the word "superpower" to "describe a system that would furnish power to the railroads and industries within the territory between Boston and Washington that has now become more familiarly known as the superpower zone." The system has become known as the superpower system. It is pointed out "first, that the economy in power production and distribution thus far attained has been due largely to the electric public utilities; second, that the failure to attain the highest possible economy has been due largely to restrictive policies that have inhibited the expansion of the electric public utilities." The plea is then made that this report, in showing the savings which may be made by the development of a larger system, may lead to the removal of present inhibitions.

Regardless of the detail organization, it is necessary that the several public utilities coöperate most closely in order to develop the fullest economy of our natural resources of coal and water-power.

SUMMARY OF CONCLUSIONS.

All data apply to the superpower zone, and for brevity this statement will be omitted in connection with the various figures given. The estimated requirement for energy supplied through the electric utilities for municipal, private and railroad purposes in 1930 is 31,000,000,000 kilowatt hours. The system proposed should supply this energy at an annual cost of $239,000,000, less than by uncoördinated systems. The total investment in the superpower system will be upwards of $1,100,000,000, of which slightly more than $400,000,000 will represent the values of existing facilities.

The saving to the manufacturing industrial establishments should be $190,000,000 in 1930 at the expense of an investment of $185,000,000 for motor equipment completely installed.

Within the superpower zone there are 36,000 miles of railroad measured as single track. Of this, 19,000 miles can profitably be electrified. The capital expenditure would be $570,000,000.

The actual saving in coal should be very great. In 1930, when the superpower system is completed, it should be 50,000,000 tons.

Various large present economical generating plants will be kept in service, whereas smaller uneconomical plants should be abandoned and provision made for the amortization of the investment.

It is suggested that the chronologic sequence for the construction of the superpower system be as follows:

Construction of steam plants in the anthracite region to use low-grade anthracite and supply power to this territory and to New York, Newark and Philadelphia.

The construction of hydro-electric plants on the Delaware and Susquehanna Rivers to supplement the above coal-burning plants.

The development of the Hudson River water-powers in the Adirondacks.

The construction of various steam plants at tide-water; and lastly,

The partial development of the Potomac River above Washington.

The water-power in this territory is comparatively small, and proper condensing water precludes further development of "mine-mouth plants" than are suggested above for the anthracite district.

For the long transmissions of large blocks of power the use of 220,000 volts is proposed. A lower voltage interconnecting network will also be necessary, and that proposed has been based on the use of 110,000 volts. The report gives many plates showing the plants and transmission lines proposed.

In the superpower zone there are now 558 electric-utility plants with an average capacity of 7900 K. W. The capacities of the superpower system plants proposed range from 60,000 to 300,000 K. W.

It is emphasized again that the superpower system is not to compete with the existing electric utilities. It is for the purpose of creating the fullest economy by coöperation of all electric utilities.

In determining the physical data on which the report and system were founded it was necessary to take the last year for which complete information was available. This was the year 1919. From the data for that and previous years the study was carried forward for ten years to 1930 to give time for the construction of the system and also to insure a design capable of caring for future growth.

The summary report is followed by thirteen appendixes dealing with electric utilities in independent operation in the superpower zone in 1919; proposed electrification of heavy traction railroads in the superpower zone; industry in the superpower zone; performance and cost of the superpower system and various other subjects relating to the problem.

The reading of this volume, "A Superpower System for the Region between Boston and Washington," should inspire any one to a greater appreciation of the necessities and possibilities of logical, technical determination of the future requirements of this great and growing industrial country.

H. GOODWIN, JR.

LABORATORY MANUAL OF PHYSICAL CHEMISTRY. By Albert W. Davison and Henry S. Van Klooster, Rensselaer Polytechnic Institute. 182 pages, illustrations, 8vo. New York, John Wiley and Sons, Incorporated, 1922.

The well-known technical institution with which the authors of this book are connected numbers among its graduates many men who have distinguished themselves in the several departments of engineering. Its professors have been prominent in both research and teaching. Elderly chemists remember with pleasure Elderhorst's work on the blowpipe, so admirably adapted for the beginner in that department of analysis. The work before us is, as stated in the title, a laboratory manual only. It is assumed that before using it the student has been well instructed in the principles of physical chemistry, and the experiments selected are mainly with a view to their bearing on engineering applications. Very extensive references to the literature are made, for the general subject and for each experiment. Descriptions of apparatus are brief, inasmuch as such information can be obtained elsewhere. Blank pages and several pages of cross-section paper are included, for note-taking and records. Whether these inclusions are advisable is a matter of doubt. The use of them may oblige the student to keep the book upon the table on which the experiments are being conducted, and thus expose it to injury, though it is true that physical chemistry, as a rule, does not involve so much "mussiness" as the regular chemical course, especially the so-called "qualitative analysis" which is usual in college and school laboratories. The reviewer, however, regards separate note-books and cross-section sheets as better.

The book is the result of large experience on the part of the authors, and constitutes an excellent manual for instruction in the extensive, important and difficult field of physical chemistry. It is well printed in large, distinct type and the line illustrations are well drawn. There is no index, which seems to be a serious omission, although for the manner in which the book is to be used, namely, in regular succession of the several items, the index is less important than in a book of reference or of study.

HENRY LEFFMANN.

LA TELEFONIA A GRANDE DIZTANZA ED I REPETITORI TELFONICI. By Dott. Annibale Craveri e Comm. Sisto Demaldé. 416 pages, 124 illustrations, 16mo. Turin and Genoa. S. Lattes and Co., 1922. Price 24 lire, net.

Italy enjoys the honor of having among its long list of distinguished scientists several of those most famous in electrical discovery. The names of Volta and Galvani are written into the history of early research, and the former has his name immortalized by being given to an important electrical unit. In recent years the name of Marconi has become familiar over all the world. Under the spur of unity and the liberal government of the House of Savoy, Italy has acquired a high standing in all departments of science, politics, statesmanship, to supplement its long prominence in music, literature and art. The satiric remark of Metternich, that "it is not a country, but a geographical expression," no longer holds. The enormous extension that has taken place in the last few years in the application of electricity to the transmission of sound has been a spur to the making of many books. The work in hand is really, as we are informed in the preface, a second edition; although not so designated on the title-page. The first edition appeared in 1919, on the occasion of the first installation of certain apparatus in Italy. It is a well-printed, compact volume of convenient pocket size, neatly bound in green cloth with gold lettering, and contains, in its 416 pages of text and 124 illustrations, a comprehensive statement of the art and science in the field to which it is devoted. The authors are familiar with the theory as well as the practice of the subject, being officers in the operative departments of the government lines. Frequent quotations from the literature of other countries show that they have not limited their studies to their own language. It is interesting to note the difference in the custom of the Italian language and English in treatment of proper names used as adjectives. English retains the capitalization, but most of the Continental languages do not. Hence, in this book we read of "linee pupinizzate" and "linee krarupizzate," which seem, to our standard, not to do full honor to Pupin and Krarup, but American chemists now frequently write "bunsen burner." The absence of an index is a serious defect of the book, but this is common in works printed on the Continent. In this case the defect is accentuated by the fact that a very scanty table of contents is provided. A good deal of attention is given to historical development of the subject, and to explanation of the principles involved, so that the book will be a great aid to the Italian student as well as to the practical worker. French scientific works are often praised for their clearness, but this book shows that Italian is capable of clear expression also. The truth is that every highly developed language is able to express all phases of thought of which the human mind is capable. Those persons who assert that some other language expresses thought better than English are simply not thoroughly familiar with the resources of the latter. HENRY LEFFMANN.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS. Report No. 126, Aeronautic Instruments, Section II—Altitude Instruments, by A. H. Mears, H. B. Hendrickson and W. G. Brombacher. Sixty-four pages, illustrations, quarto. Washington, Government Printing Office, 1922.

This report, in four parts, covers the general field of altitude instruments and closely related subjects.

Part I, on altimeters and barographs, discusses briefly the subject of barometric altitude determination. A detailed description is given of the principal types of instruments used in England, France, Germany, Italy, Denmark and America.

Part II, on precision altimeter design, deals with the errors of altimeters in general and states the principles of design and some of the instances where more precise indications are required.

Part III, on statoscopes and rate of climb indicators, mentions the uses of these instruments and presents a detailed study of the various types and methods of testing used.

Part IV, on aerographic instruments, mentions the various mechanisms and devices used in thermograph construction and describes several typical instruments. Meteorographs of various types and strut thermometers, and their uses, are included.

Report No. 131, Aerial Navigation and Navigating Instruments, by H. N. Eaton. Forty-four pages, illustrations, quarto. Washington, Government Printing Office, 1922.

This work outlines briefly the methods of aerial navigation which have been evolved during the past years and describes the instruments used.

Dead reckoning, the most universal method of navigation, is first discussed. Then follows an outline of the principles of navigation by astronomical observation, a discussion of the practical use of natural horizons, such as sea, land, cloud, and haze in making sextant observations; the use of artificial horizons, including the bubble, pendulum, and gyroscopic types; and a description of the rapid methods and the special instruments which have been devised to expedite the reduction of observations and the plotting of position. Lastly, the comparatively recent development of the radio direction finder and its application to navigation are discussed.

Report No. 132, Recent Developments and Outstanding Problems, by Franklin L. Hunt. Ten pages, quarto. Washington, Government Printing Office, 1922.

This is the concluding number of a series of reports on aeronautic instruments and discusses briefly some of the more recent developments in aeronautic instrument design and mentions some of the outstanding problems.

The different types of instruments are discussed as far as possible in the order in which they are described in the preceding reports. Among the instruments considered are precision altimeters and barographs, a thermometric altimeter which automatically corrects for the effect of air temperature on altitude readings, rate of climb recorders, a combined statoscope and rate of climb indicator, low-speed air-speed indicators for lighter-than-air craft, ground-speed indicators, gyroscopic turn indicators, navigating instruments; also special investigations relating to the altitude effect of air-speed indicators, the properties of elastic diaphragms, Bourbon tubes and bimetallic bars and ink substitute for recording instruments.

Among the outstanding problems are mentioned the need of navigating instruments for long-distance flights and for flying at night and landing in fog, the improvement of oxygen instruments for high altitude flying, and the attainment of greater reliability and precision in all aeronautic instruments.

Report No. 148, The Pressure Distribution Over the Horizontal Tail Surfaces of an Airplane, III, by F. H. Norton and W. G. Brown. Twenty-five pages, illustrations, quarto. Washington, Government Printing Office, 1922.

The authors deal with the distribution of pressure during accelerated flight of the full-sized airplane, for the purpose of determining the magnitude of the tail and fuselage stresses in stunting.

As the pressures to be measured in accelerated flight change in value with great rapidity, it was found that the liquid manometer used in the first part of this investigation would not be at all suitable under these conditions; so it was necessary to design and construct a new manometer containing a large number of recording diaphragm gauges for these measurements. Sixty openings on the tail surfaces were connected to this manometer and continuous records of pressures for each pair of holes were taken during various manœuvres. There were also recorded, simultaneously with the pressures, the normal acceleration at the centre of gravity and the angular position of all the controls.

The present investigation consisted in measuring on a standard rigged JN4H airplane the distribution of pressure over the whole of the horizontal tail surfaces while the airplane was being put through manœuvres as violently as it was thought safe, including spinning and pulling out of dives.

PUBLICATIONS RECEIVED.

Discours et Mélanges par Émile Picard, Secrétaire Perpétuel de l'Academie des Sciences. 293 pages, 8vo. Paris, Gauthier-Villars et Cie., 1922. Price, paper, 10 Francs.

The Properties of Electrically Conducting Systems, including Electrolytes and Metals, by Charles A. Kraus, Professor of Chemistry in Clark University. American Chemical Society, Monograph Series. 415 pages, illustrations, 8vo. New York, The Chemical Catalog Company, Inc., 1922. Price, $4.50.

The Chemistry and Technology of Gelatine and Glue, by Robert Herman Bogue, M.S., Ph.D. 644 pages, 8vo. New York, McGraw-Hill Book Company, 1922.

Laboratory Manual of Physical Chemistry, by Albert W. Davison and Henry S. Van Klooster. 182 pages, illustrations, 8vo. New York, John Wiley and Sons, Inc., 1922.

La Telefonia a Grande Distanza ed i Ripetitori Telefonici: Dott-Annibale Craveri e Comm. Sisto Demaldè. 417 pages, illustrations, folding plates, 12mo. Torino, S. Lattes & C., 1922.

Lefax Radio Handbook, by J. H. Dellinger and L. E. Whittemore. 8 sections, unpaged, illustrations, 16mo. Philadelphia, Lefax, Inc., 1922.

U. S. Bureau of Mines: Bulletin 192, Carbon Black—Its Manufacture, Properties and Uses, by R. O. Neal and G. St. J. Perrott. 95 pages, 8vo. Technical Paper 277, Application of the Geophone to Mining Operations, by Alan Leighton. 33 pages, illustrations, plates, 8vo. Technical Paper 311, Factors in the Spontaneous Combustion of Coal, by O. P. Hood. 9 pages, 8vo. Washington, Government Printing Office, 1922.

National Advisory Committee for Aeronautics: Technical Notes, No. 88, Test of Oil-scraper Piston Ring and Piston Fitted with Oil-drain Holes, by H. S. McDewell. 10 pages, illustrations, quarto. No. 102, Skin Frictional Resistance of Plane Surfaces in Air. Abstract of Recent German Tests, with Notes, by W. S. Diehl. 4 pages, illustrations, quarto. No. 106, Notes on Aerodynamic Forces—III. The Aerodynamic Forces on Airships, by Max M. Munk. 8 pages, illustrations, quarto. No. 107, Structural Safety during Curved Flight, by Dr. Adolf Rohrbach. 18 pages, illustrations, plates, quarto. Washington, Committee, 1922.

Municipal Sanitary Precautions During Epidemic of Influenza: Rambling thoughts of a civil engineer, by Dr. Wm. Paul Gerhard, C.E. 8 pages, 8vo. Reprinted from *Municipal and County Engineering,* April and May, 1922. Price, 30 cents.

U. S. Bureau of the Census: Fourteenth census of the United States. Manufactures, 1919. Electrical Machinery Apparatus and Supplies. Engines, Locomotives and Aircraft. Prepared under the supervision of Eugene F. Hartley, Chief Statistician for Manufactures. 2 pamphlets, quarto. Washington, Government Printing Office, 1922.

CURRENT TOPICS.

Potency of Commercial Vitamine Preparations.—E. V. McCollum and Nina Simmonds, of Johns Hopkins University (*Jour. Am. Med. Asso.*, 1922, lxxviii, 1953–1957), have tested six commercial vitamine products for vitamine B. Young rats were used as experimental animals; they were given a restricted basal diet for several weeks, then received the same diet plus a commercial vitamine preparation for an additional period of several weeks. The growth curve of each rat was determined. The rats usually gained in weight but little if at all during the administration of the vitamine preparations. The deduction is made that the commercial preparations did not contain vitamine B in concentrated form, McCollum and Simmonds recommended that milk and leafy vegetables be used to supplement the deficiencies in the ordinary diet and to insure an adequate supply of vitamines. Salads should be eaten twice daily. A liberal helping of greens and a quart of milk or its equivalent in the form of manufactured dairy products should also be taken daily.

J. S. H.

Insecticidal Spraying from an Aeroplane. (*The Chemist and Druggist*, July 8, 1922, 38).—Publicity has been given in the daily press to an experiment carried out on a Kentish farm in spraying orchards from above, carrying the outfit in a swiftly moving aeroplane. We learn from Craven & Co., agricultural chemists, Evesham, that they were consulted by the farmer, who found that his 50-acre apple plantation was suffering from a visitation of green caterpillar. A 'plane from the Haviland Company was secured, and this was fitted with a specially made blowing appliance, by means of which the whole plantation was thoroughly treated in about half an hour. It is obviously impossible to treat thoroughly a plantation in half an hour by the most up-to-date appliances working from the ground. The experiment has aroused the greatest interest among fruit and hop growers all over the country.

R.

Use of Arsenotungstic Acid in Analytic Chemistry.—While many complex inorganic acids have been prepared by various investigators, uses have been found for comparatively few of these acids. Arseno-18-tungstic acid—hitherto without a use—has been applied for the colorimetric determination of uric acid by J. Lucien Morris and A. Garrard Macleod, of Western Reserve University (*Jour. Biol. Chem.*, 1922, l, 55–63). The uric acid is isolated from the sample as zinc urate, which is then dissolved in dilute hydrochloric acid. When this solution is treated with a solution of arseno-18-tungstic acid, a blue color develops, which is intensified if sodium cyanide also be present. A standard solution of uric acid in a phosphate buffer solution is also treated with arseno-18-tungstic acid and sodium cyanide. The color of the unknown is compared with that of the standard in a colorimeter; and the uric acid content of the unknown is calculated.

J. S. H.

Electrochemical Theory of Physiological Processes.—From a general consideration of the structure and arrangement of the central nervous system, laboratory observations of the electrochemical reactions of the organism, and clinical evidence, G. W. CRILE (*Proc. Am. Philosophical Soc.*, 1921, lx, 546–552) concludes that man is an electrochemical mechanism. The unit structure is a nerve-cell battery and its prolongation the nerve fibre which extends through the synapse or key to the muscle or gland. When an electric current flows from the nerve cell, it closes the synapse, completes the circuit, and causes the muscle or gland to act. Activity of the body and certain diseases decrease the potential difference between the two parts of the cell, its nucleus and its cell body. The nerve-cell batteries are discharged during consciousness, and are recharged during sleep.

J. S. H.

Gas in 1920. (*U. S. Geological Survey Press Notice.*)—Although the gas-making industry had great difficulty in obtaining adequate supplies of good fuel in 1920, the quantity of gas sold was greater than ever before, amounting to nearly 500 billion cubic feet, having a value of more than $300,000,000, according to the Geological Survey. The sale of by-products by gas-making companies was also greater in 1920 than in any previous year. Over 100,000,000 gallons of tar, 55,000,000 pounds of ammonium sulphate or its equivalent, and nearly 125,000,000 gallons of light oil and other derivatives were the principal items among these by-products.

The average price of gas in 1920 was much higher than it had been for several years, averaging 16 cents a thousand cubic feet greater for coal gas and water gas and 5 cents a thousand cubic feet greater for oil gas and coke-oven gas than in 1918.

R.

A Study of the Influence of the Suspension upon the Oscillation of a Pendulum. P. LE ROLLAND. (*Ann. de Physique,* March-April, 1922.)—In a bibliography of memoirs dealing with the pendulum, such for example, as that published by the French Physical Society, 200 pages long, there are surprisingly few dealing with the motion of the pendulum as a measurer of time. The greater number of them are concerned with the determination of the length of the seconds pendulum or with a study of the oscillation of the pendulum at different places. It is to the practical phase of the pendulum that the present author directs his energies, and in order that he may not be superficial he gives more than 200 pages to an investigation of the influence of the method of suspension. By using the photographic method he is able to compare to the one millionth part the periods of two pendulums using no longer than three minutes for the actual swing. From this time onward his investigation must be known and quoted.

G. F. S.

Chemicals from Corn Cobs.—By developing new methods of extracting furfural from corn cobs, chemists of the United States Department of Agriculture have greatly reduced the cost of making this chemical, which is used in the manufacture of soluble and insoluble resins for stains, varnishes, insulating material, printing plates, and many other articles. Furfural has been made commercially from oat hulls and has been selling for about 50 cents a pound, but when made from cobs it is estimated that it can be manufactured at a cost of about 10 cents a pound. Cobs give the greatest yield of furfural of any of the common agricultural materials that contain it.

R.

Toxicity of Germanium.—The rare element germanium lies next to arsenic in the periodic system. The relative toxicity of these two elements is therefore a matter of interest. F. S. HAMMETT, J. H. MULLER, and J. E. MOWREY, JR., of the University of Pennsylvania (*Jour. Pharm. and Exp. Therapeutics,* 1922, xix, 337–342), have studied the relative toxicity of germanium dioxide and arsenious oxide when administered subcutaneously to albino rats. Arsenious oxide usually produced fatal results when given in a dose of 8 millegrams per kilogram of body weight; sublethal doses caused sloughing at the point of injection. Germanium dioxide in doses as great as 180 millegrams per kilogram of body weight produced neither death nor any apparent evidences of harmful effect; sloughing did not occur at the point of injection. With respect to toxicity, germanium resembles the tin group rather than the arsenic group of elements.

J. S. H.

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THE APPLICATION OF THERMODYNAMICS TO HETEROGENEOUS EQUILIBRIA.*

BY

GEORGE W. MOREY,

Physical Chemist, Geophysical Laboratory, Washington, D.C.

LECTURE I.

The science of physical chemistry has been developed from two standpoints: That of the kinetic theory, in which the relations between the phenomena discussed are derived by reasoning about the probable mechanism of the reactions; and that of thermodynamics, in which these relations are developed by the application of the two laws which form the basis of this science. These two laws in their simplest form are but the expression of fundamental relationships which are obvious common sense. The first states that when energy is transformed from one manifestation to another, none of it is lost; that all of the energy can be accounted for in one form or another. When coal is burned to heat a boiler to generate steam to run a steam engine to run a dynamo to generate electricity to charge a storage battery, only a small proportion of the energy of the coal becomes stored up in the battery. The rest has not vanished without a trace; we can follow each stage in the process, and see that in

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the boiler room some energy passes off in the stack gases, some by radiation and conduction, and some is delivered to the engine in the steam. Here again we have part of the energy bound in the steam transformed into heat which is transferred to the surroundings by radiation and conduction, part is discharged by the condensed water, and a part is transformed into mechanical work. In the last stage of the process cited, some of the electrical energy is transformed into heat, some does chemical work and is bound by the storage cell. Thus, the energy of the chemical reaction of combustion of the coal has been transformed into heat, mechanical, electrical, and again into chemical energy, and in each stage a balance can be struck showing what has become of all the energy delivered to that stage. The first law of thermodynamics merely states what we are all aware of, that all the energy that is put into a system can be accounted for in some manner, none disappearing.

The second law of thermodynamics is also fundamentally a simple concept. Its general statement has been made in many different forms, such as that heat will not of itself flow from a colder to a warmer body. That is one useful point of view. All expressions emphasize the fundamental fact that heat energy is different from other manifestations of energy; mechanical work can be completely transformed into heat energy, but heat energy cannot be completely transformed into mechanical work; electrical energy can be transformed quantitatively into heat, but a supply of heat energy cannot be transformed into electrical energy without some loss as heat energy. In every transformation of energy a certain amount is dissipated as heat, and practically every operation proceeds in such a manner that as large a proportion of its energy as is possible under the conditions prevailing is dissipated as heat, and, furthermore, the process continues until as large a proportion as is possible under the conditions of pressure, volume, and temperature has been transformed into heat. But this heat energy is not as a rule available for doing work. In some cases, as in the discharged steam from a simple steam engine, there is still some available energy, but ultimately in this case also a proportion of the heat energy is at the temperature of the surroundings and is therefore not available as a source of work. Any process, then, that takes place without the addition of energy from an outside source goes on in such a manner and to such a condition that as large a proportion as is possible of its energy is " run down," and the " run-down-ness " of the system may be taken as a measure of the extent to which the process has taken place. The two laws may be combined in the statement that in any isolated system, that is, in any combination of substances so placed that energy, either in the form of heat or work, is neither lost nor gained, the energy is constant, but it will tend to get into as run-down a condition as is possible.

This is the qualitative expression of the two laws of thermodynamics, but much more can be gotten out of them by considering their quantitative aspect. Before treating of the quantitative phase, I wish to emphasize the fact that they are true laws, laws which have been tested innumerable times, and always found to be completely true. As long as we introduce no further assumptions, the conclusions reached from thermodynamics are unexceptionable. Whenever we find conclusions deduced by thermodynamic methods that are not in complete accord with facts, such as many of the laws of dilute solutions and the mass law, we must examine the assumptions which have been made. For this reason the thermodynamic methods of attacking chemical problems laid down by Gibbs are, in my opinion, of especial value because of the fact that in all cases we are so close to our fundamental assumptions, and any further assumptions made must be made explicitly. It is not easy to slip in a vitiating assumption unwittingly. There is one point which I wish to mention before proceeding to the quantitative expression of the two laws of thermodynamics, namely, that while I have emphasized the fact that these two laws are primarily the result of experience, at the same time they are deducible from the most general principles of statistical mechanics. Gibbs has shown that they result directly from the application of the laws of probability to a system of particles numerous enough to justify the application of these laws, that is, to a " canonical ensemble." Historically, however, they are empirical experience laws, and for most purposes this is probably the best way in which to consider them.

I have already stated the first law of thermodynamics in the form of the law of conservation of energy; all the energy that is added to a system can be accounted for as doing work or as stored up in the system. If heat be added to a system, part of it may do work and the rest of it will be stored up in the system as so-called "intrinsic" energy. The intrinsic energy represents the energy bound by the system; it can all be converted into heat by proper change in the experimental conditions. If we add a small amount of heat, dQ, to a system which does work by expansion against an external pressure, p, the first law states that

$$dQ = d\epsilon + pdV,$$

the heat added, dQ, is partly converted into work, pdV, and the rest increases the intrinsic energy of the system by an amount $d\epsilon$. In the case of a gas such as H or O, a little less than one-third is converted into work, while in the case of a liquid or solid the proportion is very much less.

The above equation may be written in the form

$$d\epsilon = dQ - pdV$$

in which the intrinsic energy is expressed as a function of the amount of heat added, dQ, and the volume. The term pdV is is of the form xdX, in which x represents the intensity factor of energy, in this case pressure, and the X represents the quantity factor of energy, in this case, dV. Both intensity and quantity factors are contained in the term dQ, but it is more convenient to have this term also of the form xdX. In the case of heat energy, temperature is the intensity factor analgous to pressure in the preceding instance. The quantity factor, analogous to the volume, is yet to be determined.

In the discussion of the qualitative statement of the second law, it was stated that the energy of any system tended to attain a state of as complete run-down-ness as possible. We are familiar with the fact that a supply of heat energy, say the latent heat of crystallization of a substance, is far more useful for doing work if at a high temperature, say 1000°, than if at a low temperature; the heat energy at room temperature is in a far more run-down condition than when at 1000°. This may be made clearer by considering a volume change taking place in a reaction; the intensity factor is pressure, and the volume change is a certain number of units, say 100 cubic centimetres. If the volume change takes place at a high pressure, say 1000 atmospheres, the work energy pdV is 100,000 c.c.-atmospheres, or 100 litre-atmospheres. But if the same volume change takes place at one atmosphere pressure, the work energy pdV is only 100 c.c.-atmospheres, or one-tenth of a litre-atmosphere. Now just consider this from another point of view. Suppose at a pressure of 1000 atmospheres we have available a volume change which furnishes us with a supply of work energy which we can measure and find to be equivalent to one litre-atmosphere, and also suppose we are unable for some reason to measure the volume change, but can only measure the pressure and the work energy set free. Obviously, we can calculate the volume change from the relation

$$1 \text{ litre-atmosphere} = 1000 \text{ atmospheres times } x \text{ litres}$$
$$x = 1/1000$$

or one one-thousandth of a litre, or 1 c.c. We cannot calculate either the original or final volume, but this does not interfere with the reality of the volume concept. Similarly, if we have available the same supply of energy, one litre-atmosphere at the pressure of one hundred atmospheres, we can calculate the volume change,

$$x = 1/100 = .01 \text{ litres.}$$

The volume is much larger in this case; the work energy is in a more run-down condition. Similarly, if we have a supply of heat energy available, say from the latent heat of freezing of a substance, and this supply of heat energy, in amount one calorie, is available at 1000°, we can calculate the change in the quantity factor at this temperature just as we did the change in the quantity factor of volume energy at the pressure of 1000 atmospheres. In the case of the heat energy, we have 1 calorie = 1000° times x units of the quantity factor of heat energy, so the change in the quantity factor is 0.001 unit. If the supply of heat energy is available at 100°, the change in the quantity factor is 0.01; the heat energy is in a more run-down condition. This difference in the run-down-ness of the heat energy must be taken into consideration, and the quantity factor of heat energy must express the run-down-ness of the system. By defining the quantity factor as the quantity of heat supplied, dQ, divided by the temperature at which it is available, T, we evidently obtain a quantity which has the desired properties. The case is analogous to that of the energy expended as work against the pressure, p; the intensity factor in the one case is pressure, in the other case temperature; in the one case the work energy, $dW = pdV$, in the other case the energy is dQ; in the one case the quantity factor is the work energy dW divided by the intensity factor, p, that is $dW/p = dV$; in the other case the quantity factor is the heat energy, dQ, divided by the intensity factor, T, $dQ/T = dS$. The quantity so defined has been termed entropy, and will be designated by S. It may be regarded as a measure of the run-downness of a system. Any isolated system, that is, any system which does not gain or lose energy from its surroundings, will tend to attain to such a condition that its entropy is as great as possible; the condition of isolation implies that during the process the energy must be constant, otherwise there will be heat interchange with the surroundings, and also that the volume must be constant, otherwise there will be work interchange with the surroundings. When the system has reached such a condition that its entropy is a maximum, that is, it is as completely rundown as it is possible for it to be without change of energy or volume, it is in a state of equilibrium. When the entropy is a maximum, change in any of the conditions would result in a decrease in entropy, but our second law states that things do not of themselves go that way.

We now have found the proper substitution for dQ in the equation

$$d\epsilon = dQ - pdV;$$

it is

$$dQ = TdS,$$

in which the temperature, T, is the intensity factor of heat energy, and the entropy change, dS, is the quantity factor of heat energy. Our equation then becomes

$$d\epsilon = TdS - pdV,$$

which is the combined expression for the first and second laws of thermodynamics as usually expressed.

It is unfortunate that in dealing with the really interesting subject of the application of thermodynamics to chemical equilibrium it is necessary to devote so much time to the essentially uninteresting fundamentals of thermodynamics. It would have been much easier to start in to-day by writing down this equation, but it is usually better to start at the beginning, and I wish to emphasize the fact that in this method of treatment we are never far from the fundamentals. The rest of this lecture will be devoted to the development of the more essentially chemical aspect of the subject, and will clear the way for explicit discussion of actual systems in later lectures. To state concretely the problem before us, we wish to determine the conditions for equilibrium of a mass of matter of various kinds; in chemical problems we deal not with a one-component system such as steam or ammonia, the usual province of thermodynamics in its engineering applications, but with systems of varying degrees of complexity. We wish to determine the conditions of equilibrium of a mass of matter of different kinds, and in order to make it possible to include only such actions as we are desirous of studying, we will assume for the purpose of derivation of our equations that the mass is enclosed in a rigid and fixed envelope, which is impermeable to, and unaltered by, any of the substances enclosed, and perfectly non-conducting to heat. This gives us our isolated system, and it involves no loss in generality. This is evident from the fact that if any mass of matter were in equilibrium it would remain in equilibrium if the whole or any part of it were enclosed in an envelope as supposed. For the purpose of our discussion, we will also exclude the action of gravity, or electrical forces, and of capillarity. These factors do not come into play in the equilibria which I am going to discuss; Gibbs excludes them in his preliminary discussion, but later, one by one, removes these restrictions, and I can do no better than to refer to his classic paper for a discussion of these subjects.

When we apply the combined statement of the first and second laws to a mass of matter of invariable composition, we can express the energy as a function of the entropy and volume:

$$d\epsilon = \mathrm{T}d\mathrm{S} - pd\mathrm{V}.$$

But when the mass consists of several different kinds of matter, each independently variable, such as an aqueous solution, we must include terms to express the change of energy when the quantity of each of these is altered. The terms representing such variation must be of the form $xd\mathrm{X}$, the product of an intensity factor into the change of the quantity factor, and obviously the quantity factor is the mass of the substance added or subtracted. The intensity factor will be the rate of change of the energy of the mass as the substance is added, other variables being constant.

The intensity factors, pressure and temperature, can be considered in a similar manner. When volume is constant,

$$d\epsilon = TdS,$$

and in this case the intensity factor, temperature, is the rate of increase of energy as entropy is added;

$$d\epsilon/dS = T.$$

Similarly, when the entropy is constant, the intensity factor, pressure, is the rate of increase of energy with increase in volume,

$$d\epsilon/dV = p.$$

In the same manner we can define the intensity factor of chemical energy associated with the mass dm_1 of one component, as the rate of increase of energy with increase of m_1. Denoting this intensity factor of chemical energy by μ, we get

$$d\epsilon/dm_1 = \mu_1.$$

If we are dealing with two independently variable components, such as salt and water, we can write the complete differential of energy, the summation of all the possible ways in which the energy of the system can change, in the form

$$d\epsilon = TdS - pdV + \mu_1 dm_1 + \mu_2 dm_2,$$

in which μ_1 and m_1 refer to water, μ_2 and m_2 to salt. This is a perfectly general expression of the application of the two laws of thermodynamics to any system of two components. It can be extended to include any number of components by the inclusion of a term of the form μdm for each independently variable component. This can be expressed by writing the equation in the form

$$d\epsilon = TdS - pdV + \mu_1 dm_1 + \mu_2 dm_2 + \ldots + \mu_n dm_n.$$

It can be regarded as the fundamental equation of chemical thermodynamics, and all the laws of physical chemistry can be derived directly from this equation.

The quantity μ, the intensity factor of chemical energy, requires a few words of explanation. We give the name *chemical* *potential* to the quantity μ, and Gibbs defined it in the following words:

"If to any homogeneous mass we suppose an infinitesimal quantity of any substance to be added, the mass remaining homogeneous and its entropy and volume remaining unchanged, the increase of the energy of the mass divided by the quantity of the substance added is the potential for that substance in the mass considered."

The chemical potential has been defined for a unit weight of the substance; for a mol of the substance it is evidently the molecular weight times the quantity so defined, and the molecular chemical potential is identical with the quantity called "partial molar free energy" by Lewis. It is evidently a measure of the strength of the chemical forces which hold the substance in the homogeneous mass in question, say the solution, and subsequently I will show its relation to vapor pressure, in the case of a volatile component.

In our general equation we have terms representing the heat energy, the volume energy, and the chemical energy of each component. In considering the equilibrium relations, the intensity factors of each form of energy are of particular importance because it is necessary for equilibrium that they be uniform throughout the mass. Moreover, this is true whether our system consists only of one homogeneous mass, or whether it consists of several such masses, each uniform in composition and separated from each other by distinct surfaces of discontinuity. Such individually homogeneous parts are termed phases, and when we are considering equilibrium between several phases, it is necessary that the intensity factors, temperature, pressure, and the several potentials, shall not only be uniform in each phase, but also the same for the several phases. This appears to be self-evident; if the temperature is not uniform, it will speedily become uniform by conduction and convection; if the pressure is not uniform, it will become so by mechanical movement; and if the potential for any component is not uniform, it will become so by a re-distribution of that component. I will not go into the proof of this; Gibbs proves it explicitly, showing that it follows as a direct consequence of the application of the second law: The tendency for any system to attain a condition of as complete run-down-ness as possible, that is, the tendency for the entropy to reach maximum results in uniformity of the intensity factors, temperature, pressure, and chemical potential throughout the mass.

The equation

$$d\epsilon = \mathrm{T}d\mathrm{S} - pd\mathrm{V} + \mu_1 dm_1 + \mu_2 dm_2 + \ldots\ldots + \mu_n dm_n$$

represents the application of the combined laws of thermodynamics to a chemical system composed of several substances, such as water and salt. For direct application to chemical processes, it is usually more convenient to use an equation containing temperature and pressure as expressed variables, instead of entropy and volume, since it is usually these that we control directly. Such an equation can be derived from the preceding without the introduction of any further assumptions, and consequently it also is an expression of the application of the two laws of thermodynamics to chemical systems. The above equation may be regarded as representing the energy of an infinitesimal portion of the given mass, the total energy of the infinitesimal portion, $d\epsilon$, being regarded as the sum of the heat energy, $\mathrm{T}d\mathrm{S}$, the volume energy, $pd\mathrm{V}$, and the various chemical energies, μdm, of the infinitesimal portion of the mass. If we add up all such portions we obtain the total energy of the mass; in mathematical language, if we integrate, supposing the quantity of the mass to vary from zero to any finite value, we obtain the expression

$$\epsilon = \mathrm{TS} - p\mathrm{V} + \mu_1 m_1 + \mu_2 m_2 + \ldots\ldots + \mu_n m_n,$$

which expresses the fact that the total energy of the mass is equal to the sum of the heat energy, the volume energy, and the various chemical energies. If we now differentiate this equation in the most general manner, regarding both temperature and entropy, pressure and volume, and potential and quantity of each component, as independently variable, we get, since the differential of a product of two variables is the sum of each variable into the differential of the other, the equation

$$d\epsilon = \mathrm{T}d\mathrm{S} + \mathrm{S}d\mathrm{T} - pd\mathrm{V} - \mathrm{V}dp + \mu_1 dm_1 + m_1 d\mu_1 + \mu_2 dm_2 + m_2 d\mu_2 + \ldots\ldots + \mu_n dm_n + m_n d\mu_n.$$

If we compare this with the original equation, we see that the term $d\epsilon$ on the left side of the equation cancels the terms

$$TdS - pdV + \mu_1 dm_1 + \mu_2 dm_2 + \ldots\ldots + \mu_n dm_n$$

leaving the equation

$$0 = SdT - Vdp + m_1 d\mu_1 + m_2 d\mu_2 + \ldots\ldots + m_n d\mu_n,$$

or, as it is more conveniently written,

$$Vdp = SdT + m_1 d\mu_1 + m_2 d\mu_2 + \ldots\ldots + m_n d\mu_n.$$

This is Gibbs' equation 97.

It will be observed that this equation contains all the intensity factors, temperature, pressure, and the chemical potentials, as expressed variables, and also states that the algebraic sum of the energy changes associated with changes in these variables is equal to zero. The first equation may be considered as representing the effect of the addition of energy from outside the system; addition of an amount of energy $d\epsilon$ to the system resulted in a re-distribution of this amount of energy as heat, volume, and chemical energy. On the other hand, if a reaction takes place in the system without loss or gain of energy, it results in a change in the temperature, pressure, and the several potentials, the amount of the change in each being given by equation 97.

If we have a system composed of several components in several phases, there will be an equation of the form of 97 for each of the phases, and in each equation the intensity factors are the same, if the phases are in equilibrium. This follows from the second law. In equation 97 there are two more terms than there are components. For each independently variable component there is a term of the form $md\mu$; and if there are n components there will be n terms of this form. In addition, there are in equation 97 two other terms, Vdp and SdT, so there are $n+2$ variables for each phase. If there are two more phases than there are components, there will be $n+2$ equations between the $n+2$ variables, and the system will be completely determined; the equations can be solved and the values of all variables calculated. Such a coincidence of $n+2$ phases is only possible at a given temperature, pressure, and composition of the phases, and is termed an invariant point, and the system is said to have no degrees of freedom. If there are only $n+1$ phases, there will be $n+1$ equations between the $n+2$ variables, and if we eliminate the n potentials we have an equation between the pressure and temperature, so fixing either of these will determine the condition of the system; the system is univariant, or has one degree of freedom. With only n phases, two more restrictions must be applied, and the system is said to have two degrees of freedom. In the case of a two-component system existing in two phases, we may have any number of different solutions at a variety of temperatures, each with its own pressure, and to determine completely the state of the system we must fix two of these variables. We can fix the composition of the solution and the temperature, and then the pressure is fixed; or we can say the solution has a certain vapor pressure at a certain temperature and this will fix its composition. More generally, if p is the number of phases, n the number of components, and f the number of degrees of freedom,

$$n+2=p+f,$$

and this is the usual statement of the phase rule. This gives us a general relation between the number of components, the number of phases, and the degrees of freedom, but as we shall see later, equation 97 can give us a great deal more information than this about heterogeneous equilibria, that is, about the conditions governing equilibrium between several phases.

The simplest case of heterogeneous equilibrium is that of a one-component system, such as water, coexisting with its own vapor at a series of pressures and temperatures. In this case we have two equations of the form of 97, one for the vapor and one for the liquid, if we denote vapor and liquid by the indices v and l, respectively, these equations are

$$V^v dp = S^v dT + m^v d\mu \qquad \text{and}$$

$$V^l dp = S^l dT + m^l d\mu.$$

It will be remembered, from the derivation of these equations, that the quantities V and S refer to the total volume and total entropy of the mass considered; in this case, where there is only one component, to the total volume and entropy of the m grams contained in each phase. If we divide each equation through by the mass m, they take the form

$$v^v dp = s^v dT + d\mu$$
$$v^l dp = s^l dT + d\mu,$$

in which the lower case letters are used to denote specific volume and specific entropy, as opposed to the total volume and total entropy, denoted by the capital letters. We can eliminate $d\mu$ between these equations by simple subtraction, giving us

$$(v^v - v^l)\, dp = (s^v - s^l)\, dT,$$

or

$$dp/dT = (s^v - s^l)/(v^v - v^l).$$

Since $dS = dQ/T$ this reduces to the usual Clausius-Clapeyron equation,

$$dp/dT = dQ/T(v^v - v^l).$$

In the next lecture I will consider the application of this equation to water in more detail, and then apply equation 97 to some systems of two components.

SUMMARY.

To sum up, then, we have seen that the first and second laws of thermodynamics are primarily experience laws, the first of which is the law of conservation of energy, and the second states that energy always tends to become run-down to a less available form. The mathematical expression of the combined laws for a system of constant composition is given by the expression

$$d\epsilon = TdS - pdV,$$

in which TdS represents the heat received by the system, and pdV the work done by the system. But if we consider the system as composed of several separately variable components, the energy must be considered as a function, not only of its volume and entropy, but also of the quantities of the various independently variable components. In this case the differential of the energy may be written

$$d\epsilon = TdS - pdV + \mu_1 dm_1 + \mu_2 dm_2 + \ldots\ldots + \mu_n dm_n,$$

in which m_1, m_2, . . . m_n represent the quantities of each of the n components, and μ_1, μ_2, . . . μ_n quantities called the chemical potentials, defined as being the amount in which the energy of a homogeneous mass is increased by the addition of an infinitesimal amount of the substance in question, divided by the amount of the substance added. Integration of this equation, supposing the quantity to vary from zero to any finite amount, yields the equation

$$\epsilon = TS - pV + \mu_1 m_1 + \mu_2 m_2 \ldots. - \mu_n m_n$$

and by differentiation of this in the most general manner and comparing the result with the original equation, we get Gibbs' equation 97,

$$Vdp = SdT + m_1 d\mu_1 + m_2 d\mu_2 + \ldots - m_n d\mu_n.$$

This is a perfectly general equation between the intensity factors, of which there are, in a system of n components, n chemical potentials, and also the intensity factors, pressure and temperature; $n+2$ in all. If there are $n+2$ phases there will be $n+2$ equations of the form of 97, one for each of the phases, between the $n+2$ variables, and the system will be completely defined. If we call the number of additional restrictions which must be imposed on a system of p phases and n components the number of degrees of freedom, represented by f, we get the usual statement of the phase rule,

$$n - 2 = p + f.$$

Application of equation 97 to the equilibrium between liquid and its vapor gives the equation

$$dp/dT = (s^v - s^l)/(v^v - v^l),$$

in which the quantity factors refer to specific quantities. This is identical with the usual Clausius-Clapeyron equation.

LECTURE 2.

In the previous lecture it was shown that the two laws of thermodynamics, when applied to a system of constant composition, lead to an equation between the energy of a system and its entropy and volume,

$$d\epsilon = TdS - pdV$$

and it was pointed out that the entropy can be considered as the quantity factor of heat energy, temperature being considered as the intensity factor. When the system considered is made of several independently variable components, the energy is a function not only of the entropy and volume, but also of the masses of the several components, and the complete differential of energy is given by the equation

$$d\epsilon = \mathrm{T}d\mathrm{S} - pd\mathrm{V} + \mu_1 dm_1 + \mu_2 dm_2 + \ldots\ldots + \mu_n dm_n$$

in which the quantity μ represents the intensity factor of the chemical energy, and the condition of equilibrium is given by equality throughout the system of each of the intensity factors, temperature, pressure, and the several chemical potentials. By integration of this equation and differentiation in the most general manner and comparison with the original, the equation

$$\mathrm{V}dp = \mathrm{S}d\mathrm{T} + m_1 d\mu_1 + m_2 d\mu_2 + \ldots\ldots + m_n d\mu_n$$

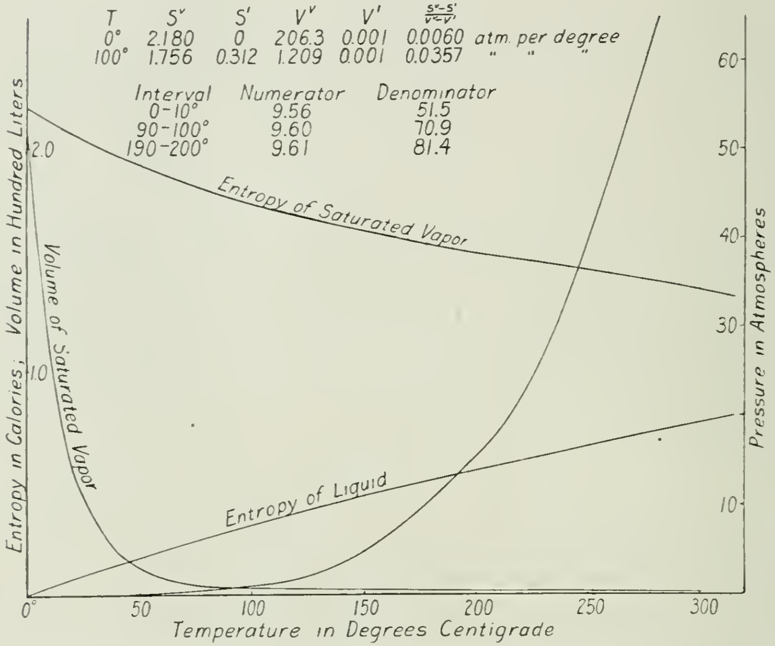
can be obtained. This also is a perfectly general consequence of the first and second laws, and from it the phase rule follows as a necessary consequence. When applied to the equilibrium between water and water vapor, we have two equations of this form, one for the liquid, the other for the vapor, and by elimination of $d\mu$ between the two equations we get an expression for the slope of the pressure-temperature curve,

$$dp/d\mathrm{T} = (s^v - s^l)/(v^v - v^l),$$

in which the entropy and volume terms denote specific quantities. It will be of interest to consider the detailed application of this equation to the pressure-temperature curve of water.

The thermodynamic properties of water are known to a considerable degree of precision, and tables giving the specific entropy and specific volume of water and steam are in common use by engineers. In such tables it is customary to take the specific entropy of liquid water at zero degrees Centigrade as zero, but since we are always dealing with differences in entropy this is immaterial. Absolute values of entropy are not determinable; to determine absolute values of entropy we would have to know the value of the entropy at absolute zero, and its variation with temperature from the absolute zero up, and we do not possess the necessary data for this. Herein lies one of the reasons for the entropy concept being a difficult one to grasp; we are not able to measure entropy directly as we are able to measure the other quantity factors volume and mass. For practical purposes, however, this is not material, since we are always dealing with entropy differences. In Fig. 1 are shown plotted the entropy of liquid water and the specific entropy of saturated water vapor from zero to 200° C., the specific volume of water vapor at the saturation pressure in the same temperature range, and the pressure-temperature curve of the equilibrium liquid-vapor. Since the slope of the P-T curve is determined by the entropy difference, it is immaterial whether the liquid curve starts at zero degrees or at some other value, since the entropy of the vapor would differ from that of the liquid by the entropy of vaporization, that is, the heat of vaporization divided by the absolute temperature, and any correction added to the liquid would also be added to the vapor. In the case of the volume, only the specific volume of the vapor is plotted, as that of the liquid is so small that it cannot be shown on the scale of the diagram. Let us now consider some actual values.

FIG. 1.



T	S^v	S'	V^v	V'	$\frac{S^v-S'}{V^v-V'}$	
0°	2.180	0	206.3	0.001	0.0060	atm. per degree
100°	1.756	0.312	1.209	0.001	0.0357	" " "

Interval	Numerator	Denominator
0-10°	9.56	51.5
90-100°	9.60	70.9
190-200°	9.61	81.4

The one-component system water, showing the change with temperature of the entropy and volume of saturated vapor, of the entropy of liquid in equilibrium with vapor, and of the saturation pressure.

At zero degrees Centigrade, if the entropy of the liquid is zero, that of the vapor is 2.18 calories. The specific volume of water vapor in equilibrium with liquid at zero degrees is 206 litres per gram; it is evident that the volume of the liquid, 1 c.c., is negligible in comparison. In the equation

$$dp/d\mathrm{T} = (s^v - s^l)/(v^v - v^l)$$

the terms must all be of the same kind; if the slope of the P-T curve is given in atmosphere per degree, and the volume in litres, the entropy must be expressed in litre-atmospheres instead of in calories. The factor for this conversion is 0.0413; inserting the above values in the equation, we get

$$dp/d\mathrm{T} = (2.180 \times 0.0413)/206 = 0.00044 \text{ atm. per degree};$$

the corresponding experimental value is the same. At 50° the values are

$$\frac{dp}{d\mathrm{T}} = \frac{(1.928-0.168)(0.0413)}{(12.02-0.001)} = 0.0060.$$

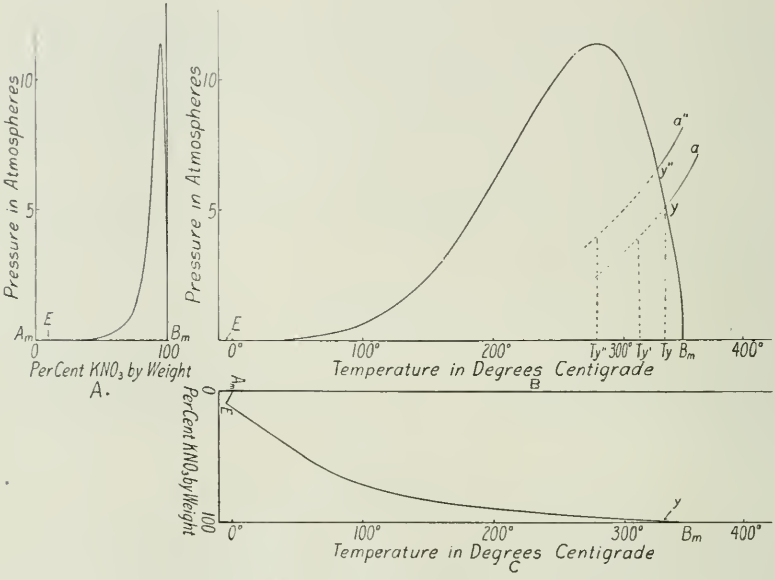
Again the experimental value is the same, and the volume of the liquid is still negligible. At 100°, the corresponding quantities are

$$\frac{dp}{d\mathrm{T}} = \frac{(1.756-0.312)(0.0413)}{(1.209-0.001)} = 0.0357,$$

agreeing exactly with experiment. In this case the value of the specific volume of the liquid amounts to less than one-tenth of one per cent. It is evident that the value of $dp/d\mathrm{T}$ is increasing with increasing temperature, and the explanation is evident from an inspection of the entropy and volume curves. As the temperature is increased the entropy of the vapor diminishes, that of the liquid increases, hence the difference decreases as the temperature increases. The numerator, the entropy of vaporization, is therefore diminishing, but its decrease is more than offset by the decrease in the denominator taking place at the same time as the result of the increasing vapor pressure increasing the density of the vapor, hence decreasing its specific volume. In the interval from zero to 10° the numerator decreases to 95.6 per cent. of its value at zero, while the denominator decreases to only 51.5 per cent. of its value at zero. The difference does not remain so marked, but for the interval 90–100° the values are 96 per cent.

and 70.9 per cent., respectively, and for the interval 190–200°, 96.1 per cent. and 81.4 per cent., respectively. Application of equation 97 to the univariant equilibrium liquid-vapor in the one-component system water shows us that not only does the pressure increase with increasing temperature, but the rate of

FIG. 2.



The binary system water-potassium nitrate. Projections of the solid pressure-temperature-concentration model on the P-X, P-T and T-X planes.

increase also increases. The P-T curve is accordingly concave upward. We will now consider the case of a simple binary system, choosing the system water-KNO_3 as illustration (Fig. 2).

The system H_2O-KNO_3 does not show liquid immiscibility, nor are solid hydrates formed, so there are four possible phases in the system; one vapor phase, one liquid phase and two solids, solid ice and solid KNO_3. Coexistence of four phases in a two-component system gives us four equations of the type of 97 between the four unknowns, pressure, temperature, and the two chemical potentials, so the system is completely determined. The four phases can only coexist at one temperature and one pressure, that is, at the invariant point, often called the cryohydrate, when one component is water. The invariant point can be considered as the intersection of four curves representing univariant equilibria, each of which equilibria will contain three of the phases which coexisted at the invariant point. We can have the four combinations ice-solution-vapor, ice-potassium-nitrate-vapor, ice-potassium-nitrate-solution, and potassium-nitrate-solution-vapor. We will consider each of these curves in detail, starting with the last, the solubility curve of potassium nitrate in water.

In the univariant equilibrium potassium-nitrate-solution-vapor there is only one phase of variable composition, the solution. Since potassium nitrate is not volatile at temperatures we are considering, the vapor phase is pure water; since potassium nitrate forms neither hydrates nor solid solutions with water, the solid phase is pure potassium nitrate. Let us now apply equation 97 to this univariant equilibrium. In the derivation of equation 97,

$$\mathrm{V}dp = \mathrm{S}d\mathrm{T} + m_1 d\mu_1 + m_2 d\mu_2$$

for a two-component system, we have expressed composition as the total mass m_1 and m_2 of the substances present, and volume and entropy as total volume and total entropy. For some purposes this is the most convenient form, but for our present discussion it is more convenient to express composition as weight per cent. potassium nitrate. Since we have $m_1 + m_2$ grams of the two components water and potassium nitrate, respectively, if we divide through by $m_1 + m_2$ we shall get

$$\frac{\mathrm{V}}{m_1 + m_2}\,dp = \frac{\mathrm{S}}{m_1 + m_2}\,d\mathrm{T} + \frac{m_1}{m_1 + m_2}\,d\mu_1 + \frac{m_2}{m_1 + m_2}\,d\mu_2\,.$$

The coefficient of the first term, the total volume divided by the total number of grams of material, is evidently the specific volume of the phase. Similarly, the coefficient of the second term is the specific entropy. The fractions

$$\frac{m_1}{m_1 + m_2} \text{ and } \frac{m_2}{m_1 + m_2}$$

are the weight fractions of the components H_2O and KNO_3, respectively, and if we represent the weight fraction of KNO_3 by x, that of H_2O will be $(1 - x)$. The equation now is

$$vdp = sd\mathrm{T} + (1 - x)\,du_1 + xd\mu_2,$$

in which v and s are specific volume and specific entropy. We will have three such equations, one for the vapor, denoted by the exponent v, one for the liquid, denoted by the exponent l, and one for the solid, denoted by the exponent s. From these equations we may eliminate $d\mu_1$ and $d\mu_2$ by the usual methods of cross-multiplication, giving the equation

$$\frac{dp}{dT} = \frac{(s^\nu - s^l) - \frac{x^\nu - x^l}{x^s - x^l}(s^s - s^l)}{(v^\nu - v^l) - \frac{x^\nu - x^l}{x^s - x^l}(v^s - v^l)}.$$

At the cryohydrate the weight fraction KNO_3 is 0.021; since the vapor is pure water, its weight fraction KNO_3 is zero, and that of the solid phase is unity. Substituting these values, we get

$$\frac{dp}{dT} = \frac{(s^\nu - s^l) + \frac{.021}{.979}(s^s - s^l)}{(v^\nu - v^l) + \frac{.021}{.979}(v^s - v^l)}.$$

The coefficient of the second term in both numerator and denominator is a fractional coefficient. Without an actual determination of the entropy of any phase, certain definite conclusions can be drawn. In the numerator, we have the entropy differences: Vapor-liquid, a positive quantity, and solid-liquid, a negative quantity. The former is always several times the latter; in the case of this dilute solution their ratio is probably not very different from the ratio of the entropy of vaporization of water to the entropy of fusion of KNO_3, of the order of magnitude of 20 to 1. The first term predominates, and the numerator is a positive quantity of the order of magnitude of the entropy of vaporization of water at zero degrees, or a little less than 2.18. In the denominator the term affected by the fractional exponent, the difference in specific volume of liquid and solid is negative and is itself very small. The first term, the volume difference vapor-liquid, is comparatively enormous; at the cryohydrate temperature and pressure it is even larger than the volume difference in pure water at its freezing point, 206 litres per gram. The slope of the pressure-temperature curve is at the beginning close to that of pure water; that of pure water is concave upward, due to the denominator decreasing in value more rapidly than the numerator, and the same is true in this case. In fact, the pressure-temperature curve of all systems containing a volatile component at low pressure will show a similar initial upward concavity, due to the rapid decrease in the specific volume of the vapor phase with increasing pressure.

As the temperature is raised, the fraction KNO_3 in the liquid increases, while the composition of the other phases remains the same. The specific entropy of the vapor continually decreases; that of the solid increases, as does that of the liquid. The first term in the numerator consequently decreases, the second increases, and the coefficient of the second term also increases; since the first term is positive, while the second is negative, the numerator is a continually decreasing positive quantity. The denominator is decreasing at a progressively slower rate. As the temperature is raised these effects continue, until a temperature is reached at which the rate of decrease of the numerator becomes equal to that of the denominator, and the curve has a point of inflection, after which it is no longer concave upward, but is concave downward; the vapor pressure of the saturated solution is still increasing with the temperature, but at a diminishing rate. The temperature of this point of inflection is approximately 145°, and the pressure is about 2.5 atmospheres.

The determination of the solubility curve of KNO_3 in H_2O is a simple matter at temperatures below 100°. As long as the vapor pressure remains less than one atmosphere, we can shake up solid and liquid in a thermostat until equilibrium is reached, suck out a sample of the supernatant liquid through a filter, and determine the composition by analysis. After the pressure has exceeded one atmosphere, other methods must be employed. Of course, if a mixture containing an excess of KNO_3 is heated in an open vessel, when the vapor pressure reaches one atmosphere the solution will begin to boil, and will evaporate to dryness. But if the mixture be heated in a closed tube, from which the water cannot evaporate, the solubility curve will be continuous until the mixture is entirely liquid; the temperature at which the saturated solution boils at a pressure of one atmosphere is not a significant point on the solubility curve. From this point of view there is no distinction between a solubility curve and a melting-point curve, and the curve EB_m can be regarded either as the solubility curve of KNO_3 in H_2O or as the melting-point curve of H_2O-KNO_3 mixtures. The first to realize this fact was Guthrie in 1886, and the system H_2O-KNO_3 was one of those which he studied. He sealed mixtures in closed tubes and observed the temperature at which the crystals disappeared. In a later lecture I will describe another method for studying solubility curves at high temperatures which can be applied over a much greater range of pressure and temperature and to a greater variety of substances than can this simple closed tube method.

As the temperature is raised past the point of inflection of the P-T curve, the KNO_3 content of the liquid increases and the coefficient of the second term in the numerator increases correspondingly. At 115°, the boiling point of the saturation solution, the ratio $x^l/(1-x^l)$ is about 2.5; at the point of inflection, about 4. As this coefficient continues to increase, the numerator decreases more and more rapidly, and the value of dp/dT decreases; but, as it is still positive, the pressure continues to increase with temperature. With a little further increase in temperature, the ratio $x^l/(1-x^l)$ becomes such that the entire second term equals the first term, and the difference is zero; the numerator is now zero, so dp/dT is zero, and the curve has a horizontal tangent. Since at this point

$$(s^v - s^l) + x^l/(1 - x^l)\ [s^s - s^l] = 0$$

it follows that

$$x^l/(1 - x^l) = -(s^v - s^l)/(s^s - s^l).$$

The ratio of the entropy difference vapor-liquid to the entropy difference solid-liquid is equal to the ratio of KNO_3 to water in the saturated solution; the saturated solution at this point contains about 95.7 per cent. KNO_3, so this ratio is approximately 95.7/4.3, or 22. The entropy of the water vapor at this temperature and pressure can be obtained from steam tables, that of KNO_3 from specific heat data, and the entropy of the liquid can accordingly be calculated. It should be remembered that we are here dealing with entropy differences, not absolute entropy, and when we take off the entropy of the steam from a steam table the assumption is made that the entropy of liquid water at its freezing point is zero. This does not diminish the usefulness of the steam tables, and neither does it interfere with the application to heterogeneous equilibria, but we must keep straight in our minds about it.

The point of maximum pressure is found at a KNO_3 content of about 95.7 per cent., a temperature of about 275°, and a pressure of about 11 atmospheres. Our equation is

$$\frac{dp}{dT} = \frac{s^v - s^l + \frac{0.957}{1 - .957}\,(s^s - s^l)}{v^v - v^l + \frac{0.957}{.043}\,(v^s - v^l)}$$

and the numerator is zero because the negative entropy difference solid-liquid, multiplied by the ratio $x^l/1-x^l$ is equal to the positive entropy difference vapor-liquid. On further increase in temperature x^l continues to increase, the negative second term becomes larger than the positive first term, and the numerator becomes negative. The denominator is still positive, so the P-T curve has a negative slope; pressure decreases with increasing temperature. On further increase in temperature, the numerator continues to become more strongly negative, until at the melting point of pure KNO_3 it is the entropy difference solid-liquid for KNO_3.

The changes which have been taking place in the denominator will now be considered. The specific volume of the vapor phase at all points is much larger than that of any other phases, its smallest value at the maximum pressure being about 100 c.c. As the pressure decreases from this point, the specific volume of the vapor increases; the effect of this is merely to alter the rate of decrease of pressure which takes place from this point. But as the liquid phase approaches KNO_3 in composition, the amount of water becoming very small, the second term in the denominator becomes of importance. The specific volume difference between fused and solid KNO_3 is but a few tenths of a cubic centimetre; when the water content is only 0.1 per cent., the negative volume difference solid-liquid is multiplied by the ratio 999/1, and at 0.01 per cent. water, by 10,000. At some small water content the large positive volume difference vapor-liquid is equalled by the much smaller negative volume difference solid-liquid, and the denominator becomes zero, the slope of the P-T curve, dp/dT, infinite. At this point the curve is vertical; on further increase in temperature the curve again has a positive slope. In a system of the type H_2O-KNO_3 the experimental realization of this portion of the curve would be extremely difficult and we will not consider it further at present, except to point out that at a zero water content the equation becomes

$$\frac{dp}{dT} = \frac{s^s - s^l}{v^s - v^l},$$

the melting-point curve of pure KNO_3. The P-T curve of the saturated solutions is therefore tangent at its end to the melting-point curve of KNO_3, the curve showing the change in melting point of potassium nitrate with pressure. This type of equilibrium will be considered later.

We have seen that a melting-point or solubility curve of the system H_2O-KNO_3 extends from the cryohydrate E to the melting point of pure KNO_3, and have followed the change in vapor pressure with composition in detail. We have therefore correlated the temperature-composition or solubility curve with the pressure-temperature curve. One curve gives the change in composition of the liquid in equilibrium with solid and vapor with the temperature, the other gives the change in vapor pressure of the saturated solution with temperature. One other pair of the three variables, composition of the liquid, temperature, and pressure, can be considered, namely, the change in vapor pressure of the saturated solution with composition. This is the pressure-composition curve; from it we see that the vapor pressure at first increases with increasing water content of the saturated solutions, reaches a maximum at a small H_2O content, then decreases rapidly with further diminution of the water content, until at its end-point at pure KNO_3 the vapor pressure is that of the triple point of KNO_3. We are all familiar with the fact that as the water content of the saturated solution increases with increasing temperature the vapor pressure increases, until at the boiling point of the solution the pressure of the atmosphere is reached. But there are two saturated solutions whose vapor pressure is one atmosphere; one has a water content of 29 per cent., the other of only one per cent. At the first boiling point, addition of heat causes the solution to evaporate, liquid changing into solid and vapor. At the boiling point at higher temperature, called by Roozeboom, who discovered it, the second boiling point, the solution boils on cooling. At the second boiling point, the liquid changes into solid and vapor with evolution of heat. If a melt of KNO_3, saturated at its melting point with water, be quickly cooled, it will be seen to boil suddenly and violently, and at the same time to solidify. This second boiling point has been observed in many systems, including silicate systems at high temperatures.

We have considered but one of the four univariant equilibria which proceed from the invariant point, the univariant equilibrium solid KNO_3-solution-vapor. The system ice-solution-vapor is a second equilibrium in which we have both liquid and vapor, and in this case solid and vapor have the same composition. Our equation becomes:

$$\frac{dp}{dT} = \frac{s^v - s^l - \dfrac{x^v - x^l}{x^s - x^l}(s^s - s^l)}{v^v - v^l - \dfrac{x^v - x^l}{x^s - x^l}(v^s - v^l)}$$

and, since $x^v = x^s = 0$,

$$\frac{dp}{dT} = \frac{s^v - s^l - \dfrac{0 - x^l}{0 - x^l}(s^s - s^l)}{v^v - v^l - \dfrac{0 - x^l}{0 - x^l}(v^s - v^l)}.$$

Cancelling, this becomes

$$\frac{dp}{dT} = \frac{s^v - s^s}{v^v - v^s}.$$

But this is the equation of the vapor-pressure curve of ice; all terms relating to the liquid have disappeared. This is a general relation; whenever any two phases in a binary system have the same composition the pressure-temperature relations become those of these two phases, without reference to the composition of the other phase present.

The preceding univariant equilibria have been formed by the disappearance of ice or of KNO_3, respectively; two more can be obtained, by the disappearance of liquid or of vapor. In case the liquid disappears, we have left ice, KNO_3, and water vapor, and the P-T curve of this equilibrium will coincide with the vapor-pressure curve of ice, and from the invariant point will go to lower pressure and lower temperature. In case the vapor disappears we have the condensed system ice-KNO_3-liquid, and the curve gives the change in eutectic composition with pressure. The equation of this curve is

$$\frac{dp}{dT} = \frac{s^{ice} - s^{l} - \dfrac{x^{ice} - x^{l}}{x^{KNO_3} - x^{l}}\,(s^{KNO_3} - s^{l})}{v^{ice} - v^{l} - \dfrac{x^{ice} - x^{l}}{x^{KNO_3} - x^{l}}\,(v^{KNO_3} - v^{l})}$$

and since $x^{ice} = 0$, $x^{KNO_3} = 1$, and $x^{l} = .021$, this becomes

$$\frac{dp}{dT} = \frac{s^{ice} - s^{l} + \dfrac{.021}{.979}\,(s^{KNO_3} - s^{l})}{v^{ice} - v^{l} + \dfrac{.021}{.979}\,(v^{KNO_3} - v^{l})}.$$

Here again the entropy and volume changes of the water are the predominating factors; since the entropy difference is positive and the volume difference, in the exceptional case of water, negative, the P-T curve of this equilibrium has a negative slope. But in this case, as in all condensed systems, the slope is very steep; the numerator is of the order of magnitude of 0.3 cal, or 0.012 litre-atmospheres; the denominator is of the order of magnitude of 0.1 c.c., or 0.0001 litres. The value of dp/dT is thus about $-0.012/0.0001$, or 120 atmospheres per degree; the curve will be almost vertical. In other words, pressure as a rule has but little effect on the equilibrium temperature and composition, as compared with temperature.

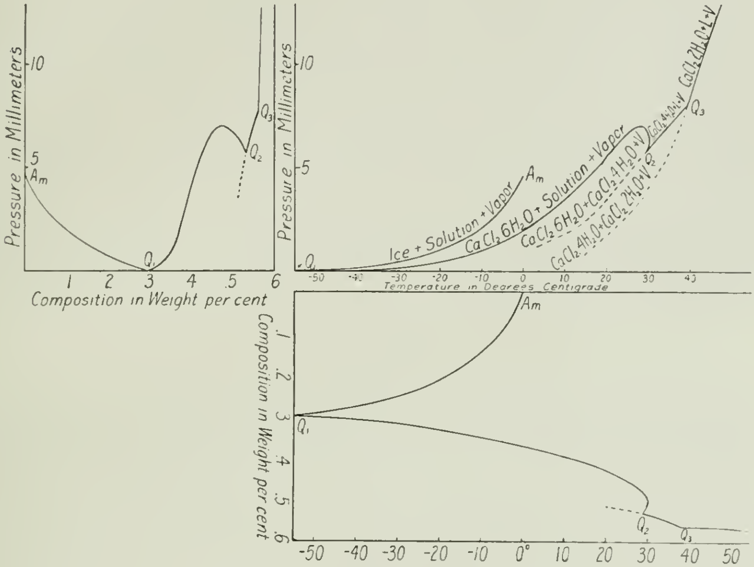
We have considered the application of equation 97 to the simplest type of system, that in which there is but one phase of variable composition, and no compounds are formed. It will be of interest to see what additional complications are introduced by the formation of compounds, and as illustration the system H_2O-$CaCl_2$ will be chosen.

The invariant point ice-$CaCl_2.6H_2O$-solution-vapor is at $-55°$, and the pressure is but a fraction of a millimetre. The compound $CaCl_2.6H_2O$ contains 50.66 per cent. $CaCl_2$, and the cryohydrate solution, 29.8 per cent. The equation of the pressure-temperature curve of the solutions saturated with $CaCl_2.6H_2O$ is

$$\frac{dp}{dT} = \frac{s^{\nu} - s^{l} + \dfrac{x^{l}}{.5066 - x^{l}}\,(s^{s} - s^{l})}{v_{\nu} - v^{l} + \dfrac{x^{l}}{.5066 - x^{l}}\,(v^{s} - v^{l})}.$$

As in the preceding case the volume change of the water vapor is the dominating factor at low temperatures, causing the curve to be concave upward (Fig. 3). As the temperature is raised the fractional coefficient of the second term becomes of increasing importance, as before, and again a point of inflection of the P-T curve is reached at 18°; the solution at this temperature contains 42 per cent. $CaCl_2$, so the coefficient of the second term is now 0.42/0.5066–0.42, or about 4.2. The curvature falls off rapidly with increase in the $CaCl_2$ content, and becomes zero at 28° and 48.5 per cent. $CaCl_2$. Since at this point

FIG. 3.



The binary system water-calcium chloride. Projections of the solid pressure-temperature-concentration model on the P-X, P-T, and T-X planes.

$$\frac{x^l}{.5066 - x^l} = \frac{s^v - s^l}{s^s - s^l}$$

the ratio of the entropy of vaporization to the entropy of solution is 0.485/0.506–0.885, or about 23 to 1. This is approximately the same ratio as was found at the point of maximum pressure in the system H_2O-KNO_3. With further increase in the $CaCl_2$ content the slope of the P-T curve becomes negative, and the pressure falls with increasing temperature.

It will be remembered that in the discussion of the preceding system it was stated that when the liquid phase was very close in composition to the solid phase, the coefficient of the second term would become large enough for the small negative volume difference solid-liquid, multiplied by the large coefficient, to equal the very much larger and positive volume difference vapor-liquid, but that the effect would be difficult to detect in such a system. When that is the case, the denominator becomes zero, the P-T curve has a vertical tangent, hence a point of maximum temperature. This is shown clearly in this system. On further increase in the $CaCl_2$ content of the solution, a maximum temperature is found, after which both temperature and pressure fall. Two effects take place very close together here; first the liquid approaches the solid so closely that the denominator becomes zero, then the two compositions become identical. When the two phases solid-liquid have the same composition, the equation of the P-T curve becomes

$$\frac{dp}{dT}=\frac{s^s-s^l}{v^s-v^l}$$

which is the equation of the melting-point curve of the hexahydrate; the condensed system liquid $CaCl_2.6H_2O$-solid $CaCl_2$-$.6H_2O$ is one of the great majority of substances that expand on melting; both the specific entropy and the specific volume of the liquid are greater than those of the solid phase. This melting point of the hydrate is called the "minimum melting point" because it is the lowest temperature at which solid and liquid of the same composition can exist together in equilibrium; a whole series of such melting points can be obtained at higher pressures in the absence of vapor, along the melting-point curve of the hydrate, the curve of the condensed system liquid-solid. It should be pointed out that this minimum melting point is not at the point of maximum temperature, but at a lower temperature. The point of maximum temperature is found at such a salt content that the denominator becomes zero, as previously stated, while the minimum melting point lies at a slightly higher salt content, and a lower temperature and pressure. In a system containing a volatile component the point of maximum temperature is not at the composition of the compound, as is the case in systems of non-volatile components or in condensed systems, but at a composition slightly displaced toward the volatile component.

In the case of $CaCl_2.6H_2O$ the difference is very small, and the two points have never been separated, but at higher temperatures and pressures the difference is no longer negligible.

After the minimum melting point has been passed, the coefficient of the second term in the denominator becomes negative, so that in both numerator and denominator the second term, the entropy and volume differences solid-liquid, in themselves negative, are multiplied by a negative coefficient, hence the second term in both becomes positive, and is to be added to the positive first terms. The slope of the P-T curve is then positive, and remains so until the invariant point $CaCl_2.6H_2O$-$CaCl_2.4H_2O$-solution-vapor is reached, at which a new solid phase, calcium chloride tetrahydrate, makes its appearance. The series of P-T curves which proceed from this invariant point when different phases disappear will be considered in the next lecture, as they present some novel features.

SUMMARY.

To sum up, we have considered in detail the application of equation 97 of Gibbs, which is itself a perfectly general expression of the two laws of thermodynamics, to the system water, and to the binary systems H_2O-KNO_3 and H_2O-$CaCl_2$. In the unary system water we found that the equilibrium vapor-liquid took place at a series of corresponding temperatures and pressures, and that the slope of the pressure-temperature curve at any point was determined by the entropy and volume differences between the two phases. The P-T curve of water is concave upward. In the system H_2O-KNO_3 we considered the four univariant equilibria which can be formed from the invariant equilibrium by disappearance of each of the four phases singly. Of these, two represented coexistence of a solid phase with solution and vapor; in that one in which ice is in equilibrium with solution and vapor, the composition changes from pure ice to the cryohydrate solution. In this equilibrium the pressure is the same as the vapor pressure of ice at the same temperature; the solution, while its composition also changes, is without influence on the pressure-temperature relations of the two remaining phases, ice and vapor. This is in consequence of a general relation, according to which in any equilibrium in which the composition of two phases becomes identical the terms relating to the remaining phase drop out of the equation for the P-T curve. The other univariant equilibrium, the univariant system KNO_3-solution-vapor, is the usual solubility curve of KNO_3 in water, along which the change in composition of the liquid is continuous from the cryohydrate to pure KNO_3. The solubility and the fusion curve are the same, and the circumstance that above the boiling point of water pressure is required to retain the water in the system is without significance in the general relationships involved. The pressure in this system at first increases with temperature, and the pressure-temperature curve is at first concave upward, due to the preponderating effect of the water. At higher temperatures it becomes concave downward, then has a horizontal tangent, then the pressure decreases with increasing temperature, and we have seen that these changes in temperature, pressure and composition are determined by the variations in the quantities in equation 97. The other two univariant equilibria which proceed from the cryohydrate are that of the condensed system ice-solution-KNO_3, which has a steep slope, and that of the system ice-vapor-KNO_3, the P-T curve of which is identical with that of ice, because of the fact that ice and vapor have the same composition. Equation 97 has also been applied to the solubility curve of $CaCl_2.6H_2O$, and the changes in composition, temperature, and pressure correlated by its aid. In this case both the temperature and the pressure have maximum values, both maxima being at a higher water content than that of the compound; and after the solution has become richer in $CaCl_2$ than the hexahydrate both temperature and pressure fall until another phase appears.

LECTURE 3.

In the preceding lectures it has been shown that application of the two laws of thermodynamics to a system composed of several independently variable components leads to the equation

$$d\epsilon = \mathrm{T}d\mathrm{S} - pd\mathrm{V} + \mu_1 dm_1 + \mu_2 dm_2 + \ldots\ldots + \mu_n dm_n,$$

in which ϵ is the total energy, $d\mathrm{S}$, $d\mathrm{V}$, dm_1, dm_2, . . . dm_n are the changes in the quantity factors, total entropy, the quantity factor of heat energy, total volume, and the quantities of the several components. The temperature, pressure, and the chemical potentials (T, p, and μ_1, μ_2, . . . μ_n) are the intensity factors of the heat, volume, and chemical energies, respectively.

From this equation, by integration and differentiation is obtained Gibbs' equation 97,

$$Vdp = SdT + m_1 d\mu_1 + m_2 d\mu_2 + \ldots\ldots + m_n d\mu_n,$$

which is also a general deduction from the two laws. Applied to a two-component system, and expressing composition as weight fraction of one component, the component of lesser volatility, the equation becomes

$$vdp = sdT + (1 + x)d\mu_1 + xd\mu_2.$$

The phase rule in its usual form is a direct consequence of this equation, and by its aid we are able to follow the changes in composition, pressure and temperature in detail, as was shown in the case of the unary system water, the binary system H_2O-KNO_3, and the binary system H_2O-$CaCl_2$. In the latter system we followed the solubility curve of the hexahydrate to the invariant point at which the tetrahydrate appears.

At this invariant point (Fig. 3) we have the four phases hexahydrate-tetrahydrate-solution-vapor, and from this invariant point four univariant equilibria are obtained by the disappearance of each, separately, of these four phases. If the liquid phase disappears we have the three phases hexahydrate-tetrahydrate-vapor; since all of these phases are of constant composition the pressure is a function of the temperature only; there is no concomitant change in composition of one of the phases. Our equation becomes

$$\frac{dp}{dT} = \frac{s^\nu - s^t - \dfrac{x^\nu - x^t}{x^h - x^t}(s^h - s^t)}{v^\nu - v^t - \dfrac{x^\nu - x^t}{x^h - x^t}(v^h - v^t)}$$; in which the exponents

h and *t* represent the hexahydrate and the tetrahydrate, respectively. Substituting the numerical values of x^v, $x^{\text{tetrahydrate}}$ and $x^{\text{hexahydrate}}$, 0, 0.6063, and 0.5066, respectively, gives the value of 6.06 as the constant coefficient of the second term. The equation now becomes

$$\frac{dp}{dT} = \frac{(s^\nu - s^t) - 6.06\,(s^h - s_t)}{(v^\nu - v^t) - 6.06\,(v^h - v^t)}.$$

The numerator of this is always positive; the entropy difference hexahydrate-tetrahydrate is negative, since the decomposition of hexahydrate into tetrahydrate and solution, to be considered later, absorbs heat, and this negative term is multiplied by a negative coefficient, making the two terms in the numerator both positive. The denominator is large and positive, because of the very large specific volume of the vapor. The value of dp/dT is consequently positive, and the pressure increases with the temperature, as is the case with the dissociation pressure of the hexahydrate. It is to be observed that this equilibrium requires the presence of both solid phases hexahydrate and tetrahydrate, which, together with the vapor, make three phases, hence three equations. The common name, dissociation-pressure curve of the hexahydrate, in this sense, is misleading; the equilibrium is the univariant equilibrium between all three phases. The invariant point is the high temperature termination of the stable portion of this curve; when a mixture of these two solids, together with vapor, is heated, at the invariant point some solution is formed; some of the solid melts to form the eutectic liquid.

A second univariant equilibrium is that formed by the disappearance of vapor. This is the condensed system composed of the two hydrates and the eutectic liquid; the composition of the eutectic liquid and the eutectic temperature both change as the pressure is increased, but the change is small, and will not be considered further.

Two univariant equilibria between solid, liquid and vapor can be formed, the solubility curves of the hexahydrate and the tetrahydrate. The first of these was considered in the last lecture; from this invariant point both temperature and pressure increase with increase in water content of the solution, and the hexahydrate has a definite melting point. At the minimum melting point solid hexahydrate melts to form a liquid of the same composition; this is called a congruent melting point.

The other equilibrium between solid, liquid and vapor is the solubility curve of the tetrahydrate. Application of equation 97 to this brings out no novel features; temperature and pressure both increase as the solution becomes richer in $CaCl_2$, and this portion of the P-T curve is concave downward over its entire course. It differs from the preceding, however, because of the circumstances that, before the point at which the P-T curve has a horizontal tangent, a new solid phase appears, calcium chloride dihydrate. This gives rise to another invariant point, at which the four phases are tetrahydrate, dihydrate, solution and vapor. In the case of the hexahydrate the invariant solution was richer in $CaCl_2$ than the compound disappearing, the solution was a eutectic, and the compound had a congruent melting point. The solution at this invariant point contains 56.4 per cent. $CaCl_2$, while the tetrahydrate contains 60.6 per cent. $CaCl_2$. Substitution of these values in our equation gives

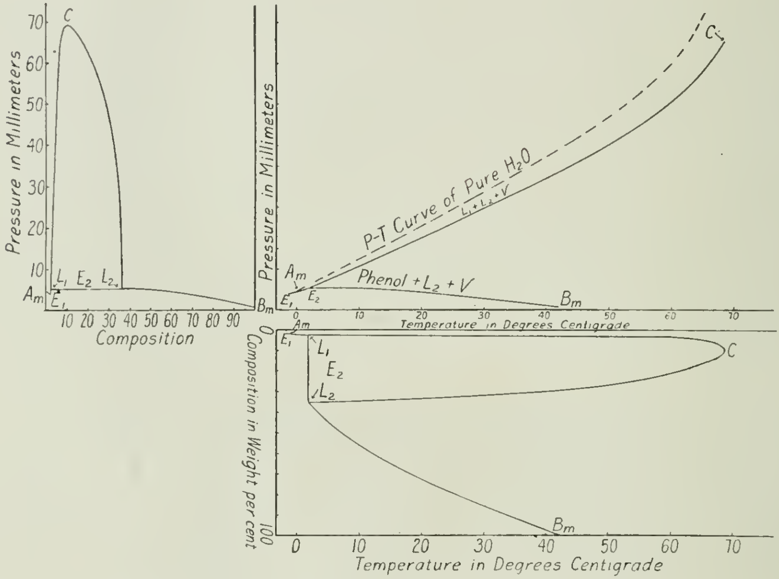
$$\frac{dp}{dT} = \frac{(s^v - s^l) + \frac{.564}{.606 - .564}(s^s - s^l)}{v^v - v^l + 13.4\,(v^s - v^l)}\;;$$

the positive entropy of vaporization is larger than the negative entropy of fusion multiplied by its coefficient, dp/dT is still positive, and both temperature and pressure are increasing along the solubility curve of the tetrahydrate at the invariant point. This solubility curve differs from the preceding in that solid and liquid do not have the same composition at any point; calcium chloride tetrahydrate has an incongruent melting point, and the invariant point is not a eutectic but a transition point. Pure hexahydrate, when heated, melts to form a liquid of its own composition; pure tetrahydrate decomposes into dihydrate and saturated solution of the composition of the solution at the invariant point.

From this invariant point three other univariant equilibria can be obtained, but they require no detailed discussion. One of them is the condensed system, whose P-T curve is almost vertical; a second is the dissociation-pressure curve of the tetrahydrate, the univariant equilibrium tetrahydrate-dihydrate-vapor; the third is the solubility curve of the dihydrate. The application of equation 97 to this equilibrium would present no new features.

The preceding illustrations have been chosen to illustrate the way in which equation 97 of Gibbs, the equation from which the phase rule was derived, can give us definite information as to the equilibrium relations in heterogeneous systems, and phase-rule studies pursued in this manner are capable of yielding much information as to the behavior of unknown systems. The cases chosen have all been simple; complications resulting from several of the phases having a variable composition have not been introduced. The vapor phase might be of variable composition; in this case x^v in our equations would no longer be zero, but would change with temperature and composition of the liquid phase. A solid phase might be of variable composition; in this case solid solution is formed, but the complications introduced are not as serious as they appear at first sight, and with the aid of equation 97 it is not difficult to fix the equilibrium relations. Also, there might be two liquid layers, both of variable composition; this case is of considerable interest, and it seems to me the usual treatment is needlessly obscure, so I will choose a system in which two liquid layers are formed, as a further example of the method of applying equation 97 to the problem of heterogeneous equilibrium.

FIG. 4.



The binary system water-phenol. Projections of the solid pressure-temperature-concentration model on the P-X, P-T, and T-X planes.

As an example of a system in which two liquid layers are formed, I have taken the system water-phenol, and in the discussion I will omit the formation of the compound that is formed between the two; this compound is not readily formed, and the equilibria between water and phenol in which the compound is not formed are the more easily obtained. The invariant point at which both ice and phenol can exist, together with solution and vapor, is at –1.2° (Fig. 4), and a small concentration of phenol, less than 1 per cent. As the temperature is raised above this point, the solubility of phenol increases slightly, until at 1.7° the saturated solution contains about 1.8 per cent. phenol. At this temperature the solid phenol in equilibrium with the solution melts, taking up water, and forming a second liquid layer. We have then four phases, solid phenol, a liquid containing 1.8 per cent. phenol, a second liquid, immiscible with the first, and containing about 36 per cent. of phenol, and a vapor phase, containing so small an amount of phenol that we may consider it as pure water. Four univariant equilibria proceed from this invariant point. The equilibrium solid phenol-solution-vapor, the solubility curve of solid phenol; and the equilibrium solid phenol-two liquids, a condensed system giving the change in the composition of the two layers in equilibrium with solid with pressure, present no new features, and will not be considered. The equilibrium between vapor, the water-rich liquid, and the phenol-rich liquid is of greater interest. At the invariant point, our equation becomes

$$\frac{dp}{d\mathrm{T}}=\frac{s^{v}-s^{l_1}-\dfrac{x^{v}-x^{l_1}}{x^{l_2}-x^{l_1}}\left(s^{l_2}-s^{l_1}\right)}{v^{v}-v^{l_1}-\dfrac{x^{v}-x^{l_1}}{x^{l_2}-x^{l_1}}\left(v^{l_2}-v^{l_1}\right)};$$

substituting the values 0, 0.018 and 0.36 for the composition of the vapor, the water-rich liquid and the phenol-rich liquid, respectively, gives us

$$\frac{dp}{d\mathrm{T}}=\frac{\left(s^{v}-s^{l_1}\right)+\dfrac{.018}{.36-.018}\left(s^{l_2}-s^{l_1}\right)}{\left(v^{v}-v^{l_1}\right)+.053\left(v^{l_2}-v^{l_1}\right)}$$

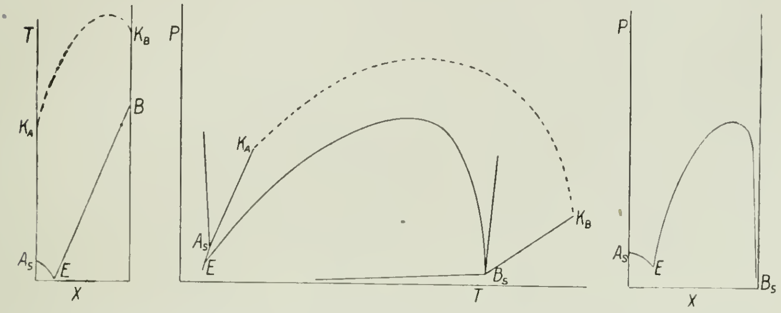
and in this case also the entropy and volume of the water is the dominating factor. The P-T curve accordingly is concave upward. As the temperature is increased, the two liquids approach each other in composition, the water-rich layer changing less than the phenol-rich layer. But at the same time their specific entropies and specific volumes approach each other, since both are liquids, composed of the same components, and increasingly close to each other in composition. For this reason the increasing value of the coefficient of the second term is offset by the decrease in the second term itself, and no maximum pressure is found. Finally, the two phases become identical in composition and properties. At the same time that the difference in composition becomes zero the difference in entropy and the difference in volume become zero, and the equation becomes indeterminate. This is as should be expected; the three-phase system was univariant because there were three equations between the three quantities—pressure, temperature, and composition. When the two liquid phases become identical, not only in composition but also in properties, there are no longer three phases, but two only, and the system is no longer univariant but divariant. In the case of calcium-chloride-hexahydrate, when the liquid and solid phases had the same composition at the minimum melting point, there was still an entropy difference, since it takes heat to melt a solid, and a volume difference; in this case all distinction between the phases disappears, and there are but two phases, liquid and vapor. At the temperature at which the two liquids merge into one another there may be not only the critical solution, but also any other mixture of liquid phenol and water; the composition of the solution or the vapor pressure must be fixed in order to completely determine the system.

The critical liquid itself is, however, completely determined. At a temperature infinitely near to the critical solution temperature of the mixture, there are still three equations, and the critical solution is determined by the additional condition that the two phases become identical. We have, then, four equations; three of the type of 97, and the additional equation expressing the condition of identity between the two liquids, so this solution is uniquely determined.

If from the invariant point solid phenol-two liquids-vapor the water-rich layer disappears, we have the univariant equilibrium solid phenol-phenol-rich liquid and vapor. This will be the case if the total phenol content of the mixture be greater than that of the phenol-rich liquid. This is another branch of the solubility curve of phenol in water, or of the melting-point curve of phenol-water mixtures, and along it the solubility of phenol in water increases uniformly, until the melting point of phenol is reached. This curve does not differ in any important respect from the upper portion of the H_2O-KNO_3 curve, except that the melting point of phenol is so much lower than that of KNO_3 that probably the vapor pressure of the solutions decrease, without first rising to a maximum.

It will not be possible to illustrate any more types of equilibria in binary systems, but I believe that enough examples have been given to show the application of this type of treatment to heterogeneous equilibria. This is in my opinion the most natural and simplest method of studying phase-rule problems, and if such problems were taken up in this manner in the text-books I believe chemists would have a clearer understanding of the fundamental problems underlying heterogeneous equilibria. As it is, there are only the two methods of approaching a problem; from the point of view of the empirical and, in most useful cases, wholly inaccurate dilute solution laws, or from the point of view of the usual statement of the phase rule as a qualitative guide in classification and outlining the problem, bolstered up by the theorem of Le Chatelier. The equation from which the phase rule was deduced is Gibbs' equation 97, and we have seen that the purely qualitative rule mentioned above is an incidental deduction from equation 97; the real meat of the equation is a quantitative guide to the changes in all the variables which define a system, and by the application of equation 97 in detail all the particulars in the behavior of a system can be predicted. Moreover, there is no restriction in the number of components to which this equation can be applied; general theorems in regard to the relations between phases may be deduced as readily for a system of n components as for a system of two components. I will give some examples of the deduction of purely general relations, and of the application of equation 97 to three-component systems, but before doing so there is an interesting point connected with the relations of systems such as water-salt at high temperatures that I desire to explain.

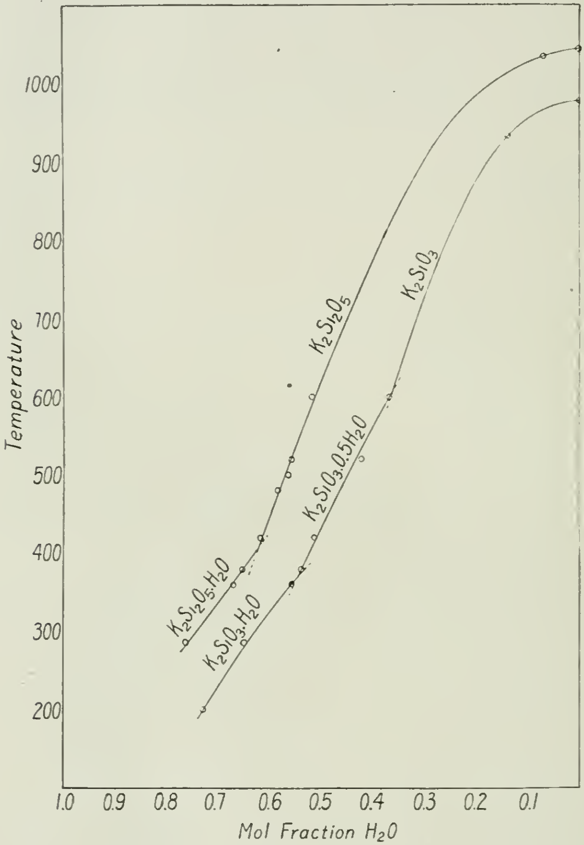
FIG. 5.



Diagrammatic temperature-concentration, pressure-temperature, and pressure-concentration projections for a binary system in which the fusion curve (EB*s*) is not intersected by the critical curve (K_AK_B).

In a binary system composed of a non-volatile and a volatile component, for example, water and a salt, the solubility or fusion curve is continuous from the eutectic to the melting point of the anhydrous component. This is shown diagrammatically in Fig. 5. At a temperature represented by the point K_A, component A shows the critical phenomena, and the critical temperature of B is at a higher temperature K_B. In this case the two curves are far apart over their entire course and no saturated solution shows the critical phenomena. This relation is shown, for example, by the systems H_2O-K_2SiO_3 and H_2O-$K_2Si_2O_5$, whose solubility relations are shown in Fig. 6. The melting points of these two compounds are both in the neighborhood of 1000°, far above the critical temperature of water, but that has no influence when the

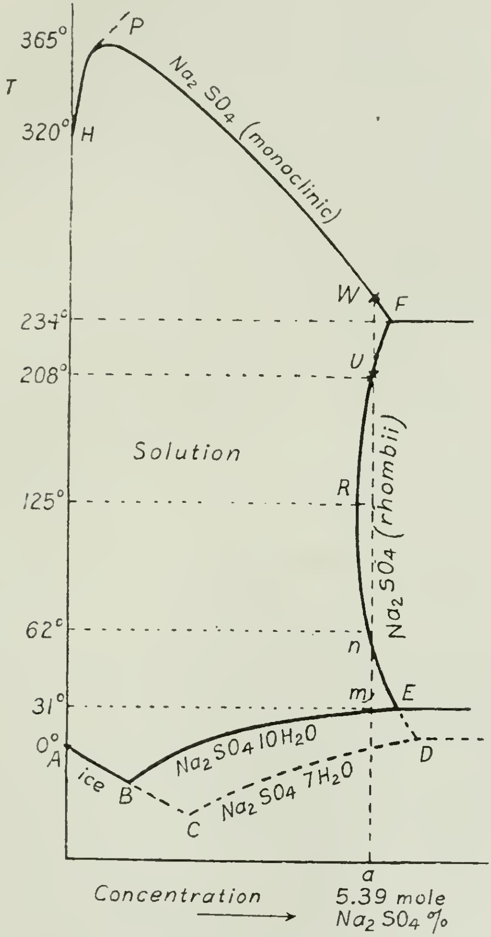
FIG. 6.



Solubility or fusion curves in the binary systems H_2O-K_2SiO_3 and H_2O-$K_2Si_2O_5$.

solubility curve and the critical curve are far apart. Critical phenomena are not exhibited by the saturated solutions; it would be necessary to heat the solutions to a much higher temperature than any along the fusion curve in order to observe critical

FIG. 7.

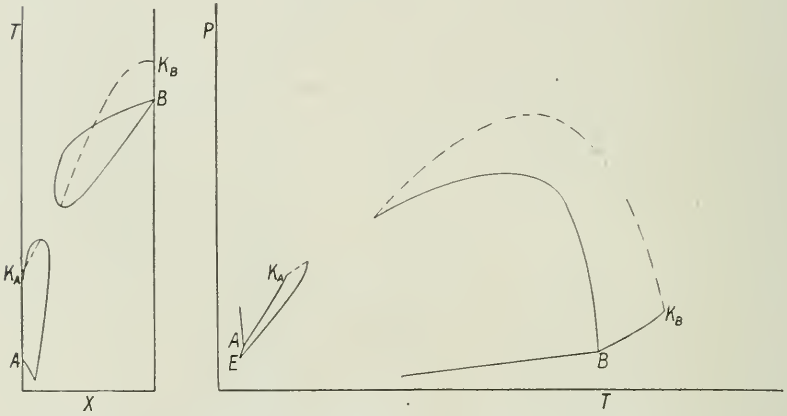


Solubility relations in the binary system H_2O-Na_2SO_4. The region of the first critical end-point has been exaggerated.

phenomena. Fig. 7 shows the variation in pressure along the saturation curve of the metasilicate and the disilicate, and it will be seen that the maximum pressure is far below the critical pressure of pure water.

In other systems, however, the critical phenomena are met with; if we consider the system water-sodium sulfate, for example, we know that the critical phenomena are shown at a temperature but slightly above the critical temperature of pure water. The low temperature portion of the solubility curve of Na_2SO_4 is shown in Fig. 7; the relations at the critical temperature are exaggerated. In the case of a solution, the critical temperature is always higher than that of the water, and it is generally, though not always, true that the critical temperature of each component is raised by the addition of the other component. In Fig. 8 the relations in a system of this type are shown diagrammatically.

FIG. 8.



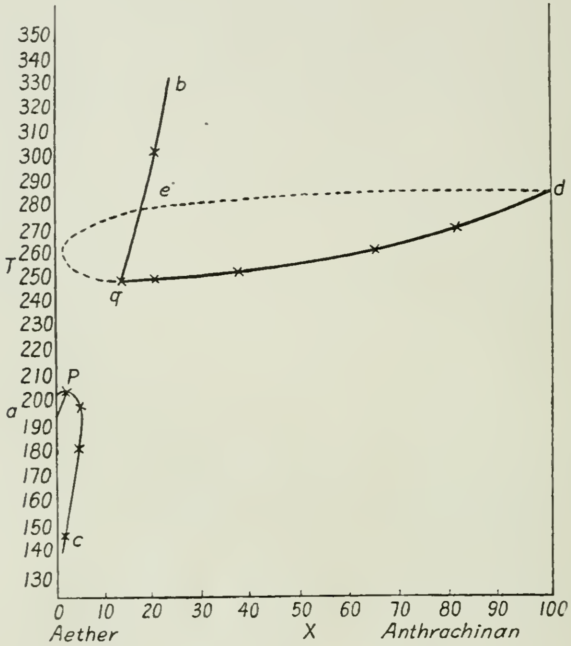
Diagrammatic temperature-concentration and pressure-temperature projections for a binary system in which the fusion curve is intersected by the critical curve (K_AK_B).

A_s is the melting point of the volatile component, or, more properly speaking, the more volatile component; and K_a is its critical temperature. Now at the critical point, liquid and vapor have identical properties; if the liquid phase is a solution containing 5 per cent. dissolved material, the vapor phase also will contain 5 per cent. of the second component. As component B is added to A, the critical temperature of A is raised, but at first the critical phenomena are shown only by unsaturated solutions. As the content of B is increased, the fusion curve and the critical curve approach each other, until a point is reached at which the critical phenomena are shown by saturated solutions; at this point there are three phases, solid, liquid, and vapor, and in addition the vapor phase and the liquid phase are identical in properties. As can be seen most readily from the pressure-temperature curve, at the critical temperature of the saturated solution the fusion curve is cut by the critical curve; this is called the first critical end-point in the system. It is evident that there must be two critical end-points. The melting point of the second component also is at a lower temperature than its critical temperature; since the critical curve is continuous from the critical temperature of one component to that of the other, and the solubility curve terminates at the melting point of the second component, if the fusion curve is cut in one point it must also be cut at a second point, at a higher temperature. At this second critical end-point also the compositions of the liquid and vapor must be the same; in the temperature-composition diagram the two curves showing the composition of the liquid and of the vapor merge into each other at the critical temperature, and at this point the resulting continuous curve has a horizontal slope. This is true of necessity at both the upper and at the lower critical end-points.

The solutions above the second critical end-point may be regarded from another point of view. In the simple system water-KNO_3, we saw that addition of water lowered the melting point of KNO_3, and also that for a certain composition range the vapor pressure of the saturated solutions increased with decreasing temperature; it required more and more pressure to keep the water on the job. The same is true in the cases in which critical end-points are formed, but in this case a point is reached at which the water can no longer be kept on the job, no matter what the pressure applied. This is analogous to the ordinary critical temperature; in the case of water, for example, as the temperature of the liquid is raised the pressure of the vapor increases, and it requires more and more pressure to keep the water liquid, until above the critical temperature it is no longer possible to liquefy the vapor by any amount of pressure. In the binary system, however, at the second critical end-point, as well as at the first, liquid and vapor have the same composition, so both components are contained in both phases. There is but one system that has been worked out of this type, the system ether-antraquinone, whose temperature-solubility relations are given in Fig. 9. The pressure-temperature relations are given in Fig. 10.

The application of equation 97 to three-component systems is merely an amplification of the methods previously applied to two-component systems, except that in this case we have one more component, one more term of the form μdm in our original equation, one more term of the form $md\mu$ in equation 97, and one more term in our expression for the slope of the pressure-temperature curve. For a two-component system, the elimination of the terms du_1, du_2 from the equations of the form of 97 for a univariant equilibrium gave the equation

FIG. 9.

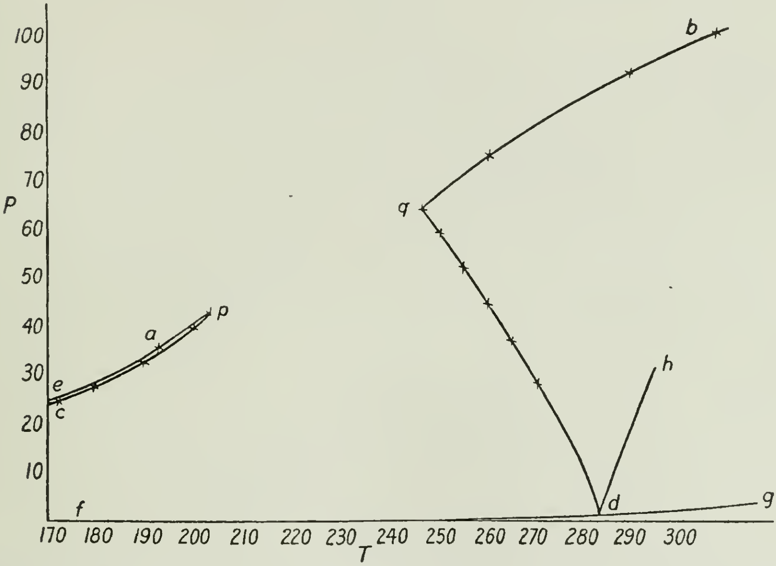


Temperature-concentration projection in the binary system ether-anthraquinone. The fusion curve *cp-qd* is intersected in the points *p* and *q* by the critical curve *bq-p*.

$$\frac{dp}{dT} = \frac{s' - s'' + \frac{x' - x''}{x''' - x''}(s''' - s'')}{v' - v'' + \frac{x' - x''}{x''' - x''}(v''' - v'')}$$

in which the composition terms represent the difference in the content of the component to which x refers, say KNO_3 in the binary system water-KNO_3, in the various phases. When the phases with single, double and triple accents are vapor, liquid and solid, respectively, the coefficients are the composition differences vapor-liquid and solid-liquid. When the compositions of the phases are plotted, as usual, along the base line of the graphical representation, the term x^v-x^l represents the length of the line x^v-x^l; the term x^s-x^l, the length of the line x^s-x^l. In three-component systems it is customary to represent the composition by means of an equilateral triangle and the amounts of the three components are represented by x, y, and $(1-x-y)$. In this case the coefficients of the entropy and volume differences between the phases, taken two by two, as before, no longer represent lengths, as in the two-component system, but areas of triangles whose apices represent the compositions of three phases. Since there are four phases, there are three entropy and volume differences, and the compositions can be represented by three areas. The equation in this case is

FIG. 10.

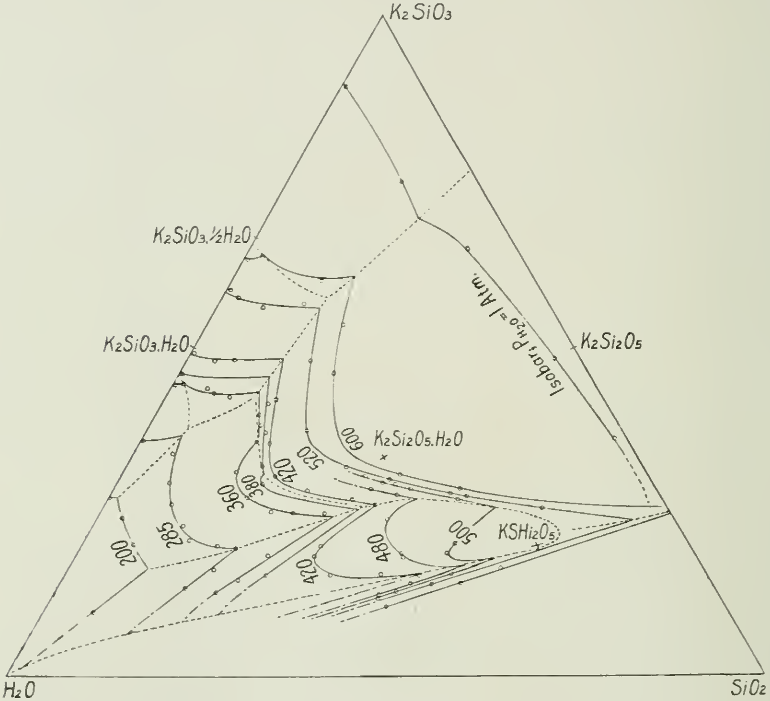


Pressure-temperature projection in the binary system ether-anthraquinone. The critical curve *eap-qb* intersects the P-T curve of the univariant equilibrium solid-liquid-vapor, *cp-qd*, in the points *p* and *q*.

$$\frac{dp}{dT}=\frac{(s'-s'')+\frac{A_{124}}{A_{234}}(s'''-s'')-\frac{A_{123}}{A_{234}}(s''''-s'')}{(v'-v'')+\frac{A_{124}}{A_{234}}(v'''-v'')-\frac{A_{123}}{A_{234}}(v''''-v'')}.$$

The course of a P-T curve in a three-component system can be followed in the same manner with the aid of this equation that it was followed in a two-component system. There is no simple example to use in illustrating the application of this equation; as far as I know, but one system of three components, one of which is volatile, has been worked out, the system H_2O-K_2SiO_3-SiO_2, which is complicated by the formation of a number of compounds. However, the vapor phase is water only, and there is no solid solution formed, so the liquid phase is the only one of variable composition. The solubility or fusion relations in this system are shown in Fig. 11; the components are H_2O, K_2SiO_3 and SiO_2, and the solubility, or, better, the saturation relations at different temperatures are shown by means of curves. A detailed discussion of this system from the point of view we have just been

FIG. 11.



Isothermal polybaric saturation curves in the ternary system H_2O-K_2SiO_3-SiO_2. An isobaric polythermal curve at 1 atm. pressure is also shown.

considering was published in the *Journal of the American Chemical Society* in January, 1918, and those interested will find there an example of the application of this method of attacking problems in heterogeneous equilibria to a complicated system, and also an illustration of the development of general laws to systems of any number of components. No one has yet worked out a four-component system in sufficient detail to afford an illustration of the theoretical treatment, but it is apparent that the extension of the methods exemplified for two and three components is not a difficult matter.

SUMMARY.

In this and the two preceding lectures we have seen that by means of the logical extension of the usual treatment of the two laws of thermodynamics to systems of several components a rigorous guide to the equilibrium relations between polyphase complexes in such systems is obtained. The method followed has been essentially that given by Gibbs in his "Equilibrium of Heterogeneous Substances," though only a small portion of that paper has been covered, merely that leading up to the derivation of equation 97. In the usual treatment of heterogeneous equilibrium the phase rule, an incidental qualitative deduction from equation 97, is used as a guide to the classification of complex equilibria, bolstered up by the theorem of Le Chatelier, a qualitative expression of the second law, in the further development with change in pressure and temperature. Equation 97 itself, however, affords not merely a qualitative, but a quantitative guide to the equilibrium relations in the most complex systems, and its detailed application serves to elucidate the most complicated relationships. The method of application of this equation has been exemplified in a series of examples, beginning with the simplest cases in one and two-component systems, then taking up in detail the more complicated cases of the formation of compounds in binary systems, both compounds with congruent and compounds with incongruent melting points, and further the formation of two liquid layers in a binary system. In addition the application to more complicated cases in both binary and ternary systems is indicated. The methods exemplified afford the most logical and natural treatment of phase-rule problems, and lead to the clearest understanding of the fundamental principles underlying heterogeneous equilibria.

LECTURE 4.

In the previous lectures I have dealt exclusively with univariant systems, systems in which there were enough phases to make possible the elimination of all the chemical potentials, giving equations which could be considered in terms of the convenient variables, pressure, temperature, and composition of the phases.

Now, an important group of laws in physical chemistry are those approximations known as the laws of dilute solutions. These laws express the fact that for sufficiently small additions of a solute, the properties of the solvent are proportional to the amount of solute present, and the usual expressions connecting the lowering of vapor pressure, lowering of the freezing point, and raising of the boiling point, are the quantitative expressions which result from the application of this fact to the processes in question.

While these laws are limited in their application to dilute solutions, there are special cases in which they give a fair approximation to the facts as determined by experiment over a considerable range of composition. Partly because of this fact, attempts have been made to extend these laws to concentrated solutions, and to explain the real deviations from these laws by assumptions as to the molecular complexity of solvent, solute, or both; assumptions which in themselves oftentimes are plausible. It should be borne in mind, however, that before we consider deviations from these laws, developed for dilute solutions, as proof that such assumptions, plausible though they may be, are in accord with facts, we should carefully examine the assumptions upon which the laws themselves are based. For this purpose a method of derivation which first develops general relations without assumptions as to the molecular condition of the components—often the point at issue—and then deduces the dilute solution approximations by means of explicit assumptions, is desirable. Such a method of treatment is indicated by Gibbs, and this lecture is an amplification of the methods used by him.

It will be observed that in all these cases we have, not three but two phases in a two-component system, and consequently the system is divariant. We have two equations of the type of 97, and hence can eliminate but one of the two chemical potentials. The laws of dilute solutions aim to provide another relation between the variables, such that the system becomes univariant; to do this it is necessary to evaluate the changes in chemical potential. The chemical potential of any component depends on the pressure, the temperature, and the composition; in a two-component system the chemical potential of the solute can be changed only by changing the pressure, the temperature, or the concentration of the solute. The total change in chemical potential is the integrated sum of the rate of change of chemical potential with change in pressure, multiplied by the amount the pressure changes; plus the rate of change with temperature, multiplied by the change in temperature; plus the rate of change of chemical potential with change in the concentration, multiplied by the change in concentration. In the form of an equation, this becomes

$$d\mu = \left(\frac{\partial\mu}{\partial p}\right) dp + \left(\frac{\partial\mu}{\partial t}\right) dt + \left(\frac{\partial\mu}{\partial x}\right) dx,$$

and our problem is to evaluate the rate of change of chemical potential with pressure, temperature, and composition, the quantities,

$$\left(\frac{\partial\mu}{\partial p}\right) \cdot \left(\frac{\partial\mu}{\partial T}\right) \cdot \left(\frac{\partial\mu}{\partial x}\right).$$

To do this we will go back to our original equations.

We have seen before that when a quantity of heat, dQ, is added to an isolated system at constant pressure, p, the energy is increased and work is done against the pressure, and the relation between the heat added, the work done, and the increase in intrinsic energy is given by the equation

$$dQ = d\epsilon + pdV.$$

For dQ, the quantity of energy added as heat, we may substitute the product of the intensity factor of heat energy, temperature, into the change in the quantity factor, entropy, and the equation becomes

$$d\epsilon = TdS - pdV.$$

This means that the total change in energy is the sum of the energy added as heat and the energy expended as work, and the intrinsic energy is expressed as a function of the entropy and volume. In case the system contains several independently variable components, the energy can be changed by changing the amount of any one of these components; the energy in this case is not only a function of the entropy and volume, but also of the mass of each component, and the equation accordingly becomes

$$d\epsilon = \mathrm{T}d\mathrm{S} - pd\mathrm{V} + \mu_1 dm_1 + \mu_2 dm_2 + \ldots\ldots + \mu^n dm_n$$

in which m_1, m_2, . . . m_n refer to the masses of the different components, μ_1, μ_2, . . . μ_n to a quantity called the chemical potential and defined as being the increase in energy of the system resulting from the addition, *dm*, of the component in question, at constant entropy, volume, and quantities of the other components. This equation may be considered as representing the energy of an infinitesimal portion of the total mass as the summation of the heat, volume, and chemical energies. It may be integrated by adding up all such similar portions of the mass, by which integration we obtain the equation

$$\epsilon = \mathrm{TS} - p\mathrm{V} + \mu_1 m_1 + \mu_2 m_2 + \ldots\ldots + \mu_n m_n.$$

If this integrated equation be again differentiated, regarding both the intensity and quantity factors as variable, and the result compared with the original equation, we get equation 97,

$$\mathrm{V}dp = \mathrm{S}d\mathrm{T} + m_1 d\mu_1 + m_2 d\mu_2 + \ldots\ldots + m_n d\mu_n.$$

There are some other thermodynamic quantities in common use which I will now define, and at the same time point out the difference in notation and nomenclature between various writers. Incidentally, the intrinsic energy, which I have denoted by the Greek letter ϵ, is oftentimes denoted by U. If to the intrinsic energy ϵ be added the work energy $p\mathrm{V}$, we get a quantity which is called the "heat content" of the system at constant pressure; this quantity was called by Gibbs the chi function, and is now commonly denoted by H:

$$\mathrm{H} = \epsilon + p\mathrm{V}$$
$$d\mathrm{H} = -\mathrm{T}d\mathrm{S} - pd\mathrm{V} + \mu_1 dm_1 + \mu_2 dm_2.$$

That this represents the heat content at constant pressure is evident from the following considerations. If we consider a system changing from one condition to another as a result of the addition of heat, and indicate the original condition by unprimed letters, the final condition by single primes, we will get for the difference in the value of H in the two states the relation

$$\mathrm{H}' - \mathrm{H} = (\epsilon' - \epsilon) + p(\mathrm{V}' - \mathrm{V})$$

since the pressure is constant. But if we turn to the equation

$$d\mathrm{Q} = d\epsilon + pd\mathrm{V}$$

we see that the change in the quantity H is numerically equal to the heat added, and is greater in the final state, after the addition of heat, than in the original state. If a reaction takes place in a calorimeter at constant pressure, the heat given out is dQ, and the value of H in the final state is less than in the original state; if dQ, positive, represents heat given out, ΔH, the change in the heat content, is negative.

Similarly, if we consider as one function the combined values of the intrinsic energy and the heat energy, we get a quantity which represents the work capacity of the system; this was called by Gibbs the psi function, and by Helmholtz the free energy, and is the quantity usually meant by the term free energy. I will call it the psi function, because of the confusion of nomenclature, as that at least cannot be confused. We have then,

$$\psi = \epsilon - TS.$$
$$d\psi = - SdT - pdV + \mu_1 dm_1 + \ldots\ldots + \mu_n dm_n.$$

That this represents the work is also evident from our original equation. If we consider that the system changes from one state to another, at constant pressure, the work done is the pressure times the change in volume:

$$p(V' - V);$$

and if we consider the difference in the psi function in the original and final state, we get

$$\psi' - \psi = (\epsilon' - \epsilon) - T(S' - S).$$

Comparing this with the original equation

$$d\epsilon = TdS - pdV, \text{ or } d\epsilon - TdS = - pdV$$

we see that the change in the quantity psi is equal to the work done by the system against pressure; when the original volume is smaller than the final volume the system has done work at the expense of its psi function or free energy, which is accordingly less, as is indicated by the negative sign.

A third thermodynamic quantity in common use is that obtained by combining the intrinsic heat and work energies into one, called by Gibbs the zeta function:

$$\zeta = \epsilon - TS + pV.$$

This is a quantity of the greatest importance; it is the quantity called by Lewis the free energy, with the difference that Lewis's free energy refers to a mol of the substance, while the zeta function as defined by Gibbs refers to a mass of $m_1 + m_2 + m_n$ grams.

If we differentiate the zeta function, considering both intensity and quantity factors as variable, we get

$$d\zeta = d\epsilon - TdS + pdV - SdT + Vdp.$$

But from the equation

$$d\epsilon = TdS - pdV + \mu_1 dm_1 + \mu_2 dm_2 + \ldots\ldots + \mu_n dm_n$$

we see that

$$d\epsilon - TdS + pdV = \mu_1 dm_1 + \mu_2 dm_2 + \mu_n dm_n,$$

so we get

$$d\zeta = Vdp - SdT + \mu_1 dm_1 + \mu_2 dm_2 + \ldots\ldots + \mu_n dm_n.$$

From this equation we can find two of the three quantities needed to fix the changes in the chemical potential of a substance, namely, the rate of change in chemical potential with pressure, $\partial\mu/\partial p$, and the rate of change of chemical potential with temperature, $\partial\mu/\partial T$. At constant temperature and constant quantities of the other components, *i.e.*, if dT, dm_2, ... dm_n are zero, we get

$$d\zeta = Vdp + \mu_1 dm_1$$

and further

$$\left(\frac{\partial\zeta}{\partial p}\right)_{Tm} = V \text{ and } \left(\frac{\partial\zeta}{\partial m}\right)_{Tpm} = \mu_1$$

in which the subscripts indicate the quantities to be taken as constant, the symbol m without subscript indicating all the masses except the one, if any, with respect to which we are differentiating. Now if we differentiate each of these again, the first with respect to m_1, the second with respect to p, we will get

$$\frac{\partial^2\zeta}{\partial p \partial m_1} = \frac{\partial V}{\partial m} \text{ and } \frac{\partial^2\zeta}{\partial m_1 \partial p} = \frac{\partial\mu_1}{\partial p}.$$

Since the order in which we differentiate is immaterial, these two quantities must be equivalent to each other:

$$\frac{\partial\mu_1}{\partial p} = \frac{\partial V}{\partial m_1}.$$

We thus have arrived at an expression for the rate of change in chemical potential with change in pressure, and find it to be equal to the rate of change of total volume with the quantity of the component, at constant temperature and mass of the other components. If we plot the volume of a solution containing 100 grams of water against the number of grams of salt, we get a curve whose slope at any point, $\frac{\partial V}{\partial m_2}$, is equal to the rate of change of chemical potential of the salt at that temperature and composition. This quantity $\frac{\partial V}{\partial m_2}$ is called by several different names. Lewis calls it the partial volume of the salt, and a more usual name is the differential volume; probably both are suggested by the fact that $\frac{\partial V}{\partial m_1}$ is a partial differential. Other writers call it the "fictive" volume, which is rather a misnomer. I prefer to call this, and other similar quantities, by the name "effective," as suggested by Doctor Williamson of our laboratory. The effective volume is exactly what the quantity really is; it is the value of the volume which is effective in considering the chemical and thermodynamic properties of the solution. Following the notation of Lewis, the quantity $\frac{\partial V}{\partial m_1}$ is often written $\bar{v}_1$; lower case, to indicate that it is a specific quantity, and with a bar over it.

The rate of change of the chemical potential with temperature may be obtained in a similar manner. If we consider the zeta function at constant pressure, we get

$$d\zeta = - SdT + \mu_1 dm_1,$$

and by again differentiating the derivative of this as before, but with respect to temperature and quantity of component m_1, we get

$$\left(\frac{\partial \mu_1}{\partial T}\right)_{pm} = - \left(\frac{\partial S}{\partial m_1}\right)_{pm} = - \bar{s}_1.$$

The rate of change of chemical potential with respect to temperature is equal to, but opposite in sign to, the rate of change of entropy with mass of the component, that is, to the "effective" entropy of m_1 in the solution. As is always the case, the entropy concept is more difficult to explain than the volume concept, though both are quantity factors of energy, but in the case of a saturated solution, the effective entropy is the differential heat of solution, the heat absorbed when one gram of the salt dissolves in a very large quantity of the almost saturated solution, divided by the absolute temperature.

We thus have evaluated two of the three rates of change of chemical potential; incidentally, we may get from this same equation, and from the original equation as well, a useful relation between the changes of chemical potential of the various components. At constant pressure and temperature, the differential of zeta is

$$d\zeta = \mu_1 dm_1 + \mu_2 dm_2 + \dots + \mu_n dm_n ,$$

and by proceeding as before we get

$$\frac{\partial\mu_1}{\partial m_2} = \frac{\partial\mu_2}{\partial m_1} .$$

But this does not give us a relation between chemical potential and concentration, and indeed such a general relation cannot be obtained on thermodynamic considerations alone. Under certain conditions the form of a possible relation is indicated by thermodynamic reasoning, and by the introduction of a number of assumptions, extraneous to thermodynamics, such a relation can be obtained.

If we apply equation 97 to a system of two components, at constant pressure and temperature, we get

$$m_1 d\mu_1 + m_2 d\mu_2 = 0.$$

If we take a constant quantity of m_1, for example water, and add a small amount of salt, dm_2, the change in the chemical potentials of water and salt is given by

$$m_1\left(\frac{\partial\mu_1}{\partial m_2}\right) + m_2\left(\frac{\partial\mu_2}{\partial m_2}\right) = 0.$$

As the solution considered is more and more dilute, m_2 approaches zero, and if we are considering the addition of the quantity of salt dm_2 to pure water, m_2 is zero. But if m_2 is zero, and the sum of the terms

$$m_1\frac{\partial\mu_1}{\partial m_2} \text{ and } m_2\frac{\partial\mu_2}{\partial m_2}$$

is to equal zero, either

$$\frac{\partial\mu_1}{\partial m_2} = 0,$$

in which case we get

$$m_1 \text{ times zero} + \text{zero times} \frac{\partial\mu_2}{\partial m_2} = \text{zero},$$

and $\frac{\partial\mu_2}{\partial m_2}$ may be a finite quantity, or, if $\frac{\partial\mu_2}{\partial m_2}$ is not zero, the first term, $m_1 \frac{\partial\mu_1}{\partial m_2}$, is not zero, and $\frac{\partial\mu_2}{\partial m_2}$ must be infinity; for only infinity multiplied by zero can equal a finite quantity.

Of these alternatives, the only possible one is that $\partial\mu_2/\partial m_2$ is infinity, in which case $\partial\mu_1/\partial m_2$ must be a finite negative quantity. It is evident that this is in accord with facts. If we have water in contact with vapor, and add salt to the water, some vapor will be condensed as the vapor pressure of the solution is lowered; the potential of water in the solution has decreased as a result of the addition of salt. As the amount of salt added be decreased to an infinitesimal amount, it is not probable that the effect of its addition would approach zero, as would be the case if $\frac{\partial\mu_1}{\partial m_2} = 0$, but it is much more probable that its effect would approach a small constant negative value, as is required if $\frac{\partial\mu_2}{\partial m_2} = \infty$. We may then consider that as the solution becomes more and more dilute, that is, as m_2 approaches zero, the value of $\frac{\partial\mu_1}{\partial m_2}$ should approach a finite negative quantity. If we replace this expression by the expression $-A/m_1$, the value of A will be positive and independent of m_1. Substituting $-A/m_1$ for $\frac{\partial\mu_1}{\partial m_2}$ we get

$$m_1\left(-\frac{A}{m_1}\right) + m_2\frac{\partial\mu_2}{\partial m_2} = 0$$

or

$$\frac{\partial\mu_2}{\partial m_2} = \frac{A}{m_2}.$$

The above has been straightforward reasoning with no assumptions, and we are therefore justified in stating that in dilute solutions the potential of the salt tends to approach a constant value of this form. Unfortunately, however, this is not of much aid; it marks the limit to which we may go on the basis of the first and second laws of thermodynamics alone.

In another place Gibbs carries the problem a step further. It can be shown that in an ideal gas—this is the first time that this much-abused term has been brought in—in an ideal gas the chemical potential μ is given by the expression

$$\mu_2 = B + AT\,ln\,\frac{m_2 v}{Vv}$$

in which B is a constant and A is the gas constant for 1 gram;

that is, R/M, in which M is the molecular weight. It is to be emphasized that A is not a universal constant, as is R. Now if we have a liquid phase in equilibrium with the gas, and if the law of Henry applies, the ratio of the concentration of the substance in the two phases is constant:

$$\frac{m_2{}^l}{Vl} = \mathrm{K}\,\frac{m_2{}^v}{Vv}.$$

We may therefore replace the ratio $\frac{m_2{}^v}{\mathrm{V}v}$ of the equation for μ by $\frac{m_2{}^l}{\mathrm{KV}l}$. Making this substitution,

$$\mu_2 = \mathrm{B} + \mathrm{AT}\,ln\,\frac{m_2{}^l}{\mathrm{KV}l}.$$

The term V^l represents the total volume of the liquid phase considered, composed of $m_1 + m_2$ grams of the two components. If we represent the specific volume of this phase by lower case v, evidently

$$Vl = (m_1 + m_2)\,v,$$

and the equation becomes

$$\mu_2 = \mathrm{B} + \mathrm{AT}\,ln\,\frac{m_2{}^l}{\mathrm{K}\,(m_1 + m_2)\,v}.$$

If now we differentiate this equation with respect to m_2, regarding v and m_1 as constant, we get

$$\frac{\partial\mu_2}{\partial m_2} = \mathrm{AT}\,\frac{m_1}{m_1 + m_2}\cdot\frac{1}{m_2}.$$

If we call $x = \frac{m_2}{m_1 + m_2}$ at constant m_1,

$$\partial x = \frac{m_1}{(m_1 + m_2)^2}\,\partial m_2;\ \partial m_2 = \frac{(m_1 + m_2)^2}{m_1}\,\partial x.$$

Substituting this value of dm_2 we get

$$\frac{\partial\mu_2}{\partial x} = \mathrm{AT}\,\frac{m_1 + m_2}{m_2} = \frac{\mathrm{AT}}{x}.$$

This gives us a value for the quantity sought, the change in chemical potential with composition, but this value is no longer free from assumption. In deriving it we assumed (1) that the vapor phase obeyed the ideal gas laws, (2) that the law of Henry applied to the distribution of m_2 between the vapor and liquid phases, and (3) that the specific volume was independent of the amount of m_2 present. But the value of A still refers to the gas constant for one gram of the vapor; van't Hoff was the first to replace this by the universal gas constant, R. To do this, we have only to remember that the molecular weight, M times the constant for one gram, gives the constant for one mol, *i.e.*, $A = R/M$. Making this substitution, we find that

$$\frac{\partial \mu_2}{\partial x} = \frac{RT}{M_2 x}.$$

Similarly, for component, m_1,

$$\frac{\partial \mu_1}{\partial x} = \frac{RT}{M_1 (1 - x)}$$

in which M_1 and M_2 are the molecular weights of the substance in the vapor. It is easy from this point to deduce the laws of dilute solutions.

Let us first consider the equilibrium between a solution of a non-volatile salt in water and derive the change in vapor pressure with composition. It is a fundamental condition of equilibrium that the chemical potential of the water must be the same in the two phases. Now the potential of water in the vapor at constant temperature depends only on the pressure of the vapor, while the potential of the water in the solution depends on the pressure and composition; since the potential of water in the two phases must remain the same, these two changes must be equal. The change in potential of water in the vapor is given by the rate of change of potential with pressure multiplied by the change in pressure, $d\mu_1^v = \left(\frac{\partial \mu_1}{\partial p}\right)^v dp \cdot$ Similarly, the change in potential in the liquid is

$$d\mu_1^l = \left(\frac{\partial \mu_1}{\partial p}\right)^l dp + \left(\frac{\partial \mu_1}{\partial x}\right)^l dx,$$

Since the two changes must be equal for the phases to remain in equilibrium

$$\left(\frac{\partial \mu_1}{\partial p}\right)^v dp = \left(\frac{\partial \mu_1}{\partial p}\right)^l dp + \left(\frac{\partial \mu_1}{\partial x}\right)^l dx.$$

But we have previously seen that

$$\frac{\partial \mu_1}{\partial p} = \frac{\partial V}{\partial m_1} - \bar{v}_1; \quad \frac{d\mu_1}{\partial x} = \frac{RT}{M_1 (1 - x)};$$

substituting,

$$\left(\bar{v}_1^v - \bar{v}_1^l\right) dp = \frac{RT}{M_1 (1 - x)} dx.$$

Since the solution is dilute, $\bar{v}_1{}^l$ for the liquid is essentially the specific volume of the liquid, and, since the vapor is pure H_2O, $\left(\frac{\partial V}{\partial m_1}\right)^v$ is the specific volume of the vapor. The specific volume of the liquid is negligible; since we have already assumed the gas laws, we may write for the specific volume of the vapor,

$$v = \frac{RT}{M_1 p}.$$

Substituting

$$\frac{RT}{M_1}\frac{dp}{p} = \frac{RT}{M_1}\frac{dx}{1-x}$$

$$d\,ln\,p = -\,d\,ln\,(1-x)\,.$$

This may be integrated, remembering that when $x = 0$, the liquid is pure water whose vapor pressure is p_0. We thus get

$$ln\,\frac{p}{p_0} = ln\,(1-x)$$

$$\frac{p}{p_0} = (1-x)$$

$$\frac{p_0 - p}{p_0} = x\,.$$

The relative lowering of the vapor pressure is equal to the percentage of salt in the solution, which is one statement of Raoult's law.

The other dilute solution approximations are as simply obtained. If we consider the lowering of the freezing point of water by a dissolved salt, we again have two phases, one of which is pure ice, the potential of which is a function of the temperature; the other a solution, the potential of water in which is a function of the temperature and the concentration. Equating the change in μ as before,

$$\left(\frac{\partial\mu}{\partial T}\right)^s dT = \left(\frac{\partial\mu}{\partial T}\right)^l dT + \left(\frac{\partial\mu}{\partial x}\right)^l dx$$

$$\frac{\partial\mu}{\partial T} = -\,\frac{\partial s}{\partial m_1} = -\,\bar{s}_1$$

$$(\bar{s}_1{}^l - \bar{s}^s)\,dT = \frac{RT}{M_1\,(1-x)}\,,$$

in which $\bar{s}_1{}^l$ is the effective entropy of water in the solution, $\bar{s}_1{}^s$, the specific entropy of ice.

If we put the effective entropy of water in the solution as equal to the specific entropy of water at the same temperature, this becomes

$$\left(s^l - s^s\right) dT = \frac{RT}{M_1(1-x)}\, dx.$$

But $(s^l - s^s) = \frac{L}{T}$, where L is the latent heat of fusion. Hence

$$L\frac{dT}{T} = \frac{RT}{M_1}\frac{dx}{1-x}, \text{ or}$$

$$\frac{dT}{T^2} = \frac{R}{M_1L}\frac{dx}{1-x}.$$

Integrating, remembering that when $x = 0$, $T = T_0$, we get

$$\left(\frac{1}{T} - \frac{1}{T_0}\right) = \frac{R}{M_1L}\, ln\,(1-x)$$

or

$$T_0 - T = \frac{RTT_0}{M_1L}\, ln\,(1-x).$$

If x is very small, x is approximately equal to $ln(1-x)$, and T differs but little from T_0. The equation then becomes

$$\triangle T = T_0 - T = \frac{RT^2}{M_1L}\, x.$$

This is the usual form for the freezing point lowering of dilute solutions. The further relations, such as the raising of the boiling point by a dissolved solute, are obtained in a similar manner.

It is evident, then, that by making certain assumptions we are able to arrive at the usual form of the dilute solution approximations; and it is also evident that as soon as we make these assumptions, the equations lose their unexceptionable character and become no more certain than the assumptions introduced. Of these, those relating to the application of the gas laws to the vapor and to the neglect of the volume of the liquid in comparison to that of the vapor, do not introduce very large errors, and the magnitude of these errors can be calculated. It will be observed that there is no assumption involved in the derivation of the first form of the approximation equation, $d\mu_2/dm_2 = A/m_2$, except that this expression is derived explicitly for the case that the quantity of the component m_2 is very small; this equation merely states that for small amounts of salt m_2, the change in the chemical potential of the water approaches a constant value, $-A/m_1$, that of the salt, A/m_2. But to identify this constant A with the universal gas constant, it is necessary to introduce some assumption, such as Henry's law. After making this assumption, Raoult's law and the usual expressions for the lowering of freezing point and raising of the boiling point follow immediately; but after all, there is very little difference between assuming Henry's law and Raoult's law. The relation expressed in the equation $\frac{\partial \mu_2}{\partial x} = \frac{RT}{M_1 x}$, or at least in the equation, $\frac{\partial \mu_2}{\partial m_2} = \frac{A}{m_2}$, undoubtedly expresses a fundamental law for dilute solutions. When we come to apply these relations to solutions which are not dilute, we get into such difficulties as are involved in trying to apply Raoult's law to a system forming two liquid layers; the vapor pressure of water is the same from the water-rich and from the water-poor layer, although these may contain as widely differing percentages of water as 99 and 1. Deviations from Raoult's and associated laws are oftentimes taken as evidence of molecular complexity of the solvent or solute, or a combination between the two, and I have no doubt that all these processes do take place. But before accepting these deviations as proof that there are such molecular rearrangements, and especially before these deviations are taken as a measure of the extent to which the process has taken place, we should bear in mind that agreement with these laws represents a particular combination of special conditions; the surprising thing is, not that the dilute solution laws are not applicable over a greater range of composition and to a greater variety of substances, but that they do give a fair approximation to the facts in so many cases. In considering a general theory of dilute solutions, we should not expect that such a theory should provide us with an exact and generally applicable expression for $d\mu/dx$, that is, that we should be able to calculate all the properties of all chemical combinations without experiment. The problem is far too complicated for that; we are unable to state the basic relationships which occasion such differences in behavior as the formation of a salt hydrate in one case and the failure of such a hydrate to form in another; or the basic relationships which occasion such differences in behavior as are shown by systems forming two liquid layers. To me, it appears best to interpret our experimental results in the light of the certain fundamental laws of thermodynamics, and by further study of systems from this point of view, possibly to arrive at some general relation which will give us a deeper insight into the mechanism of chemical action.

SUMMARY.

The underlying purpose of these lectures has been to present, in as simple a form as possible, the fundamental features of that portion of Gibbs' great paper, "Equilibrium of Heterogeneous Substances," which lead up to, and are essential to, the development of equation 97. As has been emphasized throughout, this equation is a powerful weapon for attacking the problem of equilibria between phases, and affords a more direct and simple, as well as a far more potent, attack than does the usual statement of the phase rule, which is but an incidental qualitative deduction from equation 97. By the detailed application of this equation problems of heretogeneous equilibria may be solved completely if the entropy and volume changes are known in their entirety. But more than this, by the application of this equation, and such a general knowledge of entropy and volume differences as are involved in the knowledge that a vapor phase has a greater entropy and volume than the liquid phase with which it is in equilibrium, or that the high-temperature modification of a phase has a greater entropy than the low-temperature modification, it is possible to predict, with an approach to quantitative accuracy, the behavior of the system when subjected to changes in pressure, temperature, and composition. Furthermore, this thermodynamic method is not limited in its application to two or three-component systems, but can be extended readily to include any desired number of components.

A sharp line must be drawn between those relations which are derived from the two laws of thermodynamics without the aid of further assumptions, and those whose derivation involves not only the thermodynamic laws proper, but also further assumptions extraneous to thermodynamics. To this latter clan belong the dilute solution approximations. In dealing with dilute solutions it is usual to assume some relation between composition and thermodynamic properties which will enable a divariant equilibrium such as that between ice and a dilute salt solution to be treated as a univariant equilibrium. It was shown by Gibbs that when the amount of one component approaches zero, such a relation becomes possible, and he indicated the form the relation would take. Making certain explicit assumptions, he further identified the constant value which the rate of change of the potential of water with addition of salt approaches as the amount of salt approaches zero, with the gas constant for one gram of the solute. Making these assumptions, the derivation of the ordinary dilute solution laws is easy, and this method of derivation has the advantage of confronting us squarely with the assumptions involved in these dilute solution approximations.

The Dezincification of Brass.—It has long been known that the standard brass consisting of copper and zinc will lose its zinc at a greater ratio than the copper under a variety of circumstances; even when constantly in contact with a fairly pure water, the zinc may be so completely removed as to leave nothing but a brittle porous mass of copper. Mr. Ralph B. Abrams of the senior class in Chemical Engineering, University of Wisconsin, presented a paper at the forty-second general meeting of the American Electrochemical Society in September, describing a research to determine the manner in which this removal of zinc takes place under ordinary conditions. His conclusion is as follows:

The first step is the dissolving of the brass as a whole. The copper in solution then redeposits replacing brass as a unit. This redeposition will not take place unless there is some means of holding the dissolved copper in contact with the brass. This can be accomplished in two ways, one by the presence of a membrane, the other by having a large excess of dissolved copper present. Obviously this latter possibility is a remote one, especially so far as natural conditions are concerned. The membrane may be anything whatsoever, so long as it performs the function of keeping the dissolved copper in contact with the brass. Cuprous chloride is the usual membrane. Whether or not dezincification shall take place can be controlled by merely supplying or taking away the membrane. Briefly then, the dezincification of brass is the dissolving of the brass as a whole, the holding of the dissolved copper in contact with the brass by a membrane, and the subsequent redeposition of the copper.

H. L.

STUDIES IN PHOTOGRAPHIC SENSITIVITY.

I.

THE DISTRIBUTION OF SENSITIVITY AND SIZE OF GRAIN IN PHOTOGRAPHIC EMULSIONS.*

BY

E. P. WIGHTMAN, A. P. H. TRIVELLI AND S. E. SHEPPARD.

THE problem of the "latent photographic image" has not infrequently excited curiosity and interest outside purely photographic circles. It has been an "imponderable," in some ways less susceptible of exact measurement than atom or electron. Arguments in favor of a chemical or physical nature have held the field without the deadlock being broken. To the problem of the "latent image" there has been added that of "sensitivity." On the one hand, it has been recently suggested that, at least in one and the same emulsion, this is nothing but an affair of geometry and probability.[1] Sensitivity, on this view, is only the *chance* of a grain, or connected group of grains, being hit by a light-quantum, hence, for unshadowed grains, is strictly a matter of projective area. On the other hand, chemists and emulsion-makers have arrived at a substantial theory of sensitiveness which in its most recent developments [2] tends to identify the substances of "sensitiveness" with both the latent and the developed image, as dispersed or colloid silver. As noted in more detail later, it may be assumed that in the silver bromide grain of emulsions there exists, owing to reducing conditions in preparing the emulsion, a specific, or even individual, distribution of a photocatalyst.

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* Communicated by Dr. C. E. K. Mees, Director; Communication No. 142 from the Research Laboratory of the Eastman Kodak Company.

[1] Cf. L. Silberstein: "A Quantum Theory of Photographic Exposure." Paper read before Am. Asso. Adv. Sci. (Toronto, 1921) *Phil. Mag.*, 44, 257 (1922).

[2] Lüppo-Cramer: "Kolloid-chemie u. Photographie," 2d Ed.; F. F. Renwick: *J. Soc. Chem. Ind.*, 1920, p. 156T; A. P. H. Trivelli and S. E. Sheppard: "Monograph on the Silver Bromide Grain of Photographic Emulsions," Research Laboratory of the Eastman Kodak Company; S. E. Sheppard: *Phot. J.*, 1922, p. 88.

This is very feasibly a nucleation of colloid silver amicrons, dispersed in the silver halide lattice. Differential sensitivity of grains, on this view, depends upon this distribution of sensitizing nuclei; any probability function found valid either for variation of sensitivity amongst grains of the *same size,* or relating sensitivity to size of grain, enters in the process of emulsion preparation, rather than in that of exposure.

We propose, in this and subsequent papers, to examine these hypotheses, to note wherein they lead to similar conclusions, and as far as possible to test experimentally between them. The hypothesis of a discrete structure of light is of great theoretical significance; practically, the problem posed is of fundamental importance in the photographic industry.

In this paper is presented (1) a statement of the problem, with a discussion of some previous work on the photochemical law for the silver halide grain; (2) a correlation theory of the size-frequency of photographic emulsions and their sensitometric characteristics; (3) a comparison of theories of the relation of sensitivities and size distribution to the density exposure function. The material of part (2) will be dealt with more fully in another place and connection.[3] Its presentation is necessary in order that the very varied "disperse" character of photographic emulsions may be realized, as also the broad statistical basis of the connection of grain size with emulsion speed.

I. STATEMENT OF THE PROBLEM.

It has already been pointed out that in earlier work (H. and D., etc.) consideration of individual variations of the grains of silver halide emulsions was lacking. It is now known that the elementary grains are definite crystals of one system and class, but that in a given emulsion they vary:

1. In total size or volume;
2. In cross-section or projective area;
3. In shape.

It may be further considered possible, even probable, that wide variations of "sensitivity" exist among the grains of one and the same emulsion. We may initially define "sensitivity" as the reciprocal of the energy required to make a grain developable by a developer of given reduction potential. It is generally accepted at present that the condition for developability is a nucleus, *i.e.*, that the photo-effect, whatever its nature, is localized in the grain. The most concrete development of this is that the nuclei consist of colloid silver, either provided (in part at least) by photolysis of silver halide, or formed by condensation of preexistent colloid silver amicrons to submicrons. This latter hypothesis is due to F. F. Renwick. His primary contention, that the sensitive substance is not silver halide at all, but colloid (metallic) silver has recently received support from some remarkable experiments of F. Weigert.[4] In any case, if we attribute a definite sensitivity to a grain, this means that a certain finite increment of energy is necessary for developability. In the general problem of chemical reactivity, what has been termed the *critical energy increment*[5] of a molecule is analogous to this "inertia" of the grain, the reciprocal of its sensitivity.

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[3] Cf. *J. Phy. Chem.,* in press.

Considering the variable of sensitometry, the density D, it must be remembered that to a near approximation grains contribute, on complete development, to density in proportion to their number and size conjointly, or again, to a slightly lower approximation, to their number and projective area. The quotient

$$\frac{\triangle D}{\triangle E} = \frac{\text{density increment}}{\text{energy increment}}$$

reckoned per unit area, would appear *a priori* to be independent of the size of grain, assuming a continuous wave-front. But if conditions permit a local concentration of energy related to the size of grain, the magnitude of the above quotient will depend upon the distribution of grain sizes in unit area.

Supposing a continuous wave-front, that is, *not* a quantum-like or discrete structure of radiation, local condensation of the energy to the critical increment might be effected in the material: (1) By reason of a variable distribution of a photochemical catalyst in the material, or specifically, among the grains. The probability of a grain reaching the critical increment would then depend upon its having a certain amount, and perhaps individual distribution, of the catalyst, the primary function of which would be to increase the energy density of absorbable type.[6] Colloid silver submicrons supply a concrete example. Alternatively, it may be supposed that the silver halide is itself relatively inert, and with Renwick that the colloid silver particles are the true photosensitive material. In either case, the distribution of the "catalyst" could depend on the size of the grains, *e.g.*, the probability of a grain having sufficient catalyst might be proportional to its mass. *In this case, the sensitiveness-variation curve would coincide, to a first approximation, with the size-frequency curve,* for one and the same emulsion. (2) Local condensation and a sensitivity variation might be effected, as suggested in Toy's paper,[7] by optical conditions of refraction, reflection, etc., within the grain but depending on chance orientations and concentrations of the crystalline grains. Such a hypothesis is difficult to prove or disprove, but the statistical data being accumulated may strengthen or weaken its plausibility.

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[4] *Sitz. ber preuss. Akad. Wiss.*, 1921, p. 641.

[5] W. McLewis: "System of Physical Chemistry," vol. iii, p. 140.

There remains, by exhaustion, the possibility of local, or granular, concentration of energy not by virtue of inherent factors of the sensitive material, not by accidental circumstances in its disposition, but as a necessary consequence of a discrete structure of the energy itself.[8]

The mathematical development of this assumption has been dealt with by Dr. L. Silberstein. It may, however, be pointed out here that to a large extent it gives the same relation between effective sensitivity variation and size-frequency distribution as that previously discussed on the hypothesis of a photocatalyst distributed amongst grains with a probability varying as their masses. On the quantum theory, however, it is the projective area which is fundamental rather than the mass. The important modifying factor of "clumping," or secondary aggregation of the primary grains, will be noted in connection with the results of measurements of size-frequency.

We advance later an approximate theory of the photochemical law for the single silver halide grain. Hence it appears desirable to examine more closely the experimental results of R. Slade and G. I. Higson,[9] since they propose as a result of these an empirical formula expressing "the photochemical law of the silver halide grain." Further, Higson has used these results, and this formula as a basis for deduction of density-exposure functions and ideal characteristic curves.[10] Essentially, their data consist in counts of numbers of grains in a one-grain layer made developable by increasing exposure, impressed either by increasing intensity for constant time, or by increasing time for constant intensity. They considered that in the emulsion used all the grains were of the same size, which appears doubtful to us, in view of our results with similar emulsions. But, passing this by, they advance a further postulate.[11] "All experimental evidence leads to the conclusion that all grains in one emulsion behave identically if they are of the same size." This is contrary to results of Svedberg[12] and has since been directly rebutted by Toy,[13] yet it is quite fundamental to their argument and mode of presenting their data.

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[6] Cf. W. McLewis: "System of Physical Chemistry," vol. iii, p. 140 (1919).

[7] *P. J.*, 61, 417 (1921). We may note here, in connection with the data given later, that in *thick* grains the *position* of a photocatalytic centre might vary in grains of same size and shape.

[8] Cf. F. E. Ross: *Astrophys. J.*, 52, 96 (1920).

They state,[14] "If (following Einstein) it is assumed that light is discrete in its nature, and that it is only necessary for one of these light quanta to be absorbed by a grain to make it developable, then if there were a number of grains, a, present on the plate, and they were exposed to a light of intensity, I, for a time, t, after which time x grains had been made developable,

$$\frac{dx}{dt} = kI(a-x)$$

and integrating between limits 0 to t and 0 to x

$$ln\,\frac{a}{a-x} = kIt,$$

or

$$x = a\,(1-e^{-kIt}).$$

If the grains were of different sizes, the probability of their obtaining a nucleus would vary, the larger grains being more likely to be affected; k would therefore have a different value for each size of grain.

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[9] R. Slade and G. I. Higson: *Proc. Roy. Soc.*, **98A**, 154 (1920).

[10] G. I. Higson: "The Action of Light on the Photographic Plate," *Phot. J.*, **61**, 35 (1921), and *Ibid.*, p. 144.

[11] See p. 156, *loc. cit.*

[12] The. Svedberg: *Phot. J.*, **62**, 180 (1922).

[13] F. C. Toy: *Phot. J.*, **61**, 417 (1921).

[14] See p. 157, *loc. cit.*

"The present investigation has shown that k *has* a larger value for larger grains, but also that it is not generally true that the number of grains changed is a simple function of the product It. *It is therefore impossible that the mechanism of the process is the absorption of light in discrete quanta, as has been assumed above.**

"In this investigation of the photochemical law of the silver halide grain, plates were prepared from an emulsion containing grains which were, as nearly as possible, all the same size. The emulsion was coated on the plate in such a thin layer that there was only one layer of grains. These plates were exposed either to varying intensities for the same time or to the same intensity for varying times. The source of light used was monochromatic blue light from the mercury arc in some cases, and white light (continuous spectrum) in others.

"If the total number of grains present is a, and x is the number changed after exposure for a time t, to a light of intensity, I, then

$$\frac{dx}{dt} = P(a-x),$$

where P is the probability of any grain being made developable in unit time, and is a function of I and of t.

"Integrating

$$\int_0^x \frac{dx}{a-x} = \int_0^t P \cdot dt,$$

therefore

$$\ln \frac{a}{a-x} = \int_0^t P \cdot dt,$$

"This, however, does not make it possible to evaluate P as a function of I and t without making other assumptions."

But, although an equation of the type $x = a(1 - e^{-kIt})$ is deducible by application of the discrete theory of light,[15] it is also obtained by other considerations not involving this, but simply the assumption that the grains do differ in quality, *i.e.,* inherent sensitivity. The result, if confirmed, that the above expression did not hold, would not contradict the hypothesis of sensitivity-variation —it would only show that the distribution of sensitivity assumed[16] was inadequate. When Slade and Higson proceed still to evaluate

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* Italics are ours.

$$\int_0^x \frac{dx}{a-x} = \int_0^x \frac{dN}{N-n}\, as = \int_0^t P\, dt$$

where P is "the probability of any grain being made developable in unit time and is a function of I and t," it appears to us that they thereby assume tacitly, just the contrary to their statement (p. 158), "In the emulsion used . . . all the grains were of the same size, *and experimental proof has been obtained that they were all of the same quality.*"[17] It is difficult to see—on this basis, and accepting the principle that a grain made developable is completely developed (in three minutes, under their conditions with one-grain layers)—how *any* function of the type

$$\int_0^x \frac{dx}{a-x}$$

could be evaluated. For all these grains, of identical size and "of the same quality" should become simultaneously developable for some one and the same exposure (although this unique exposure need not be that regulated by the reciprocity law $E = It =$ constant) *unless the mechanism of the process is the absorption of light in discrete quanta.* For, if grains of identical size *and quality* are exposed to radiation of discrete structure, then the "hits" will be regulated by some probability function.

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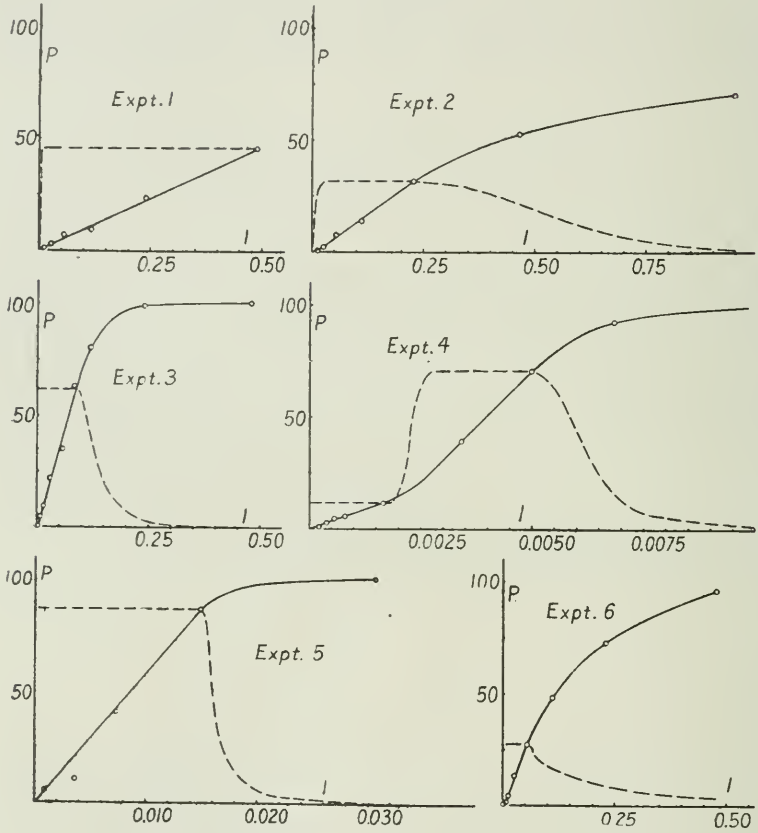
[15] Cf. F. E. Ross: *Astrophys. J.,* 52, 95 (1920).

[16] v. infra, p. 18.

[17] Our italics.

Since their premises, argument, and conclusions do not seem to fit together, it appeared desirable to reconsider their data from a different basis. Instead of forming the logarithmic quotient $ln\frac{a}{a-x}$ as dependent variable, which *assumes* either heterogeneity in the material or discreteness in the radiation—it is reasonable to plot the usual accumulation curve, *i.e.*, the number of grains changed, as ordinate, against either the *intensity*, for constant time of exposure, or the *time* for constant intensity. We have done this for Slade and Higson's data, with the results shown in Figs. 1, and 2, Intensity Scale.

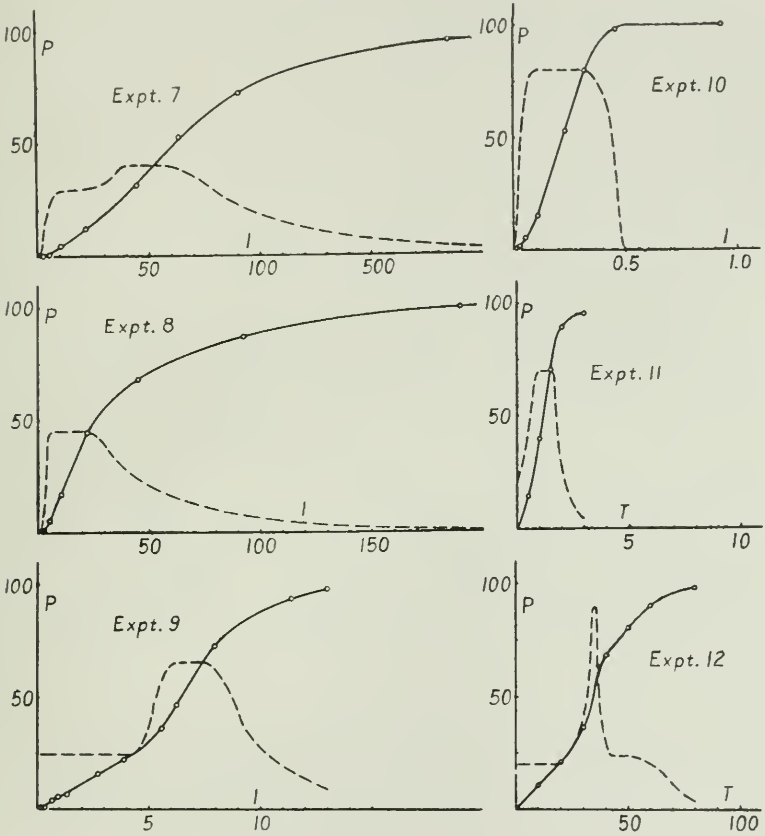
FIG. 1.



Slade and Higson's data replotted.

In experiments 1, 2 and 3 (Fig. 1) (with monochromatic Hg. blue light) it will be seen that the number of grains changed is a linear function of the intensity up to 30 per cent. or more of the total, when the "rate of change" becomes less. To bring out these features, we have also plotted the first derivatives of the curves, *i.e.*, as noted later, the "rate curves."

FIG. 2.



Slade and Higson's data replotted.

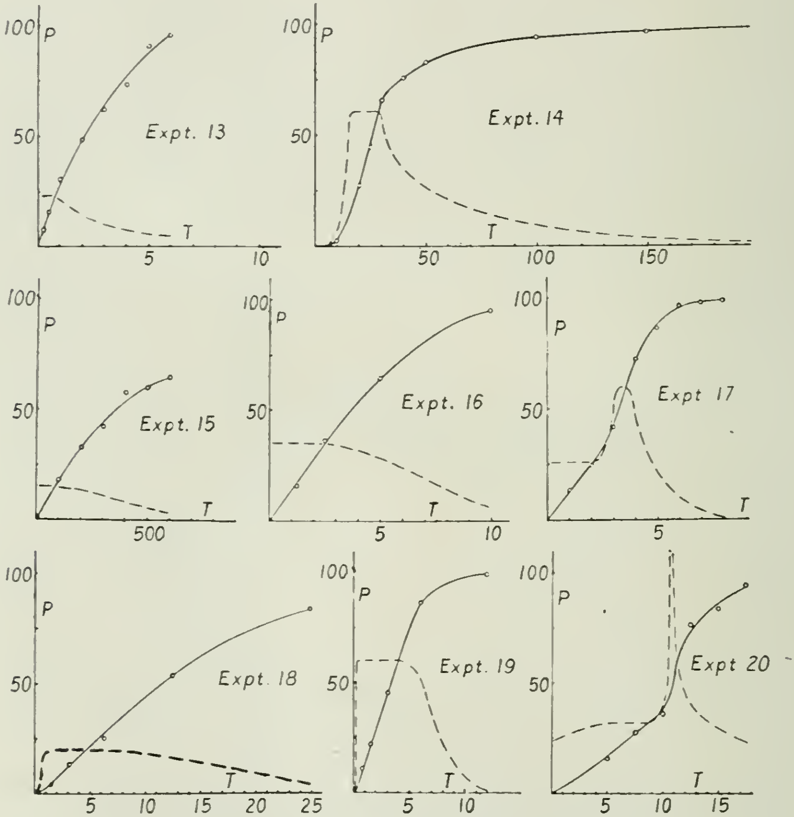
An interesting feature of these replotted curves is that the "white light" intensity curves show on the whole a greater similarity to the "monochromatic" time curves than to the "monochromatic" intensity curves. All of these show a well-marked "initial acceleration," corresponding to autocatalysis.

On the whole, the data agree with the view that the rate of photochemical change in the single grain, leading to a sufficient accumulation of the photoproduct to induce developability, follows a law of the type

$$\frac{dm}{dA} = k_1 A + k_2 f(m) A \ ,$$

where A = light absorbed, k_1 is the coefficient of absorption of

FIG. 3.



Slade and Higson's data replotted.

unchanged halide, k_2 is the coefficient of absorption of the photoproduct, $f(m)$ a function of its mass and distribution in the grain. Now we may suppose k_1 is small compared with $k_2 f(m)$, and that $f(m)$ varies initially from grain to grain. We can write

$k_2f(m) = K$ and obtain the same type of "fundamental reaction formula" (for the single grain) as noted later, in which case the "first derivative" indicates the "frequency curve of inertias." *But* the present data do point to this "frequency curve" as not being entirely inherent, *i.e.*, preëxistent to exposure, but liable to be modified and induced by exposure itself, *as would result from an autocatalytic effect* of the photoproduct varying from grain to grain. Stress has been laid on this factor by one of the writers in a recent paper on the optical sensitizing effect of soluble iodides on the silver bromide emulsion.[18] Although in the subsequent portion of this paper it is neglected, the evidence from Slade and Higson's data, while not complete, decidedly indicates that this aspect requires further consideration. The more marked occurrence of the "initial acceleration" with both the "white light" intensity curves and the "monochromatic" time curves is perhaps connected with it; photosensitizing, for the same time period, but with different intensities, would be more probable with white light pulses than with the more regular trains of waves of "monochromatic" blue light, except when these were allowed to act for increasing periods of time.

In a paper on "The Photographic Efficiency of Heterogeneous Light,"[19] F. C. Toy has given incidentally results of further experiments tending to confirm Slade and Higson's formula as to intensity. He states,[20] "Slade and Higson have shown that the relation between light intensity, I, and the effect produced A, is given by

$$A = \alpha I (1 - e^{-\beta I})$$

where α and β are constants, so that if the intensity is small, A varies as I^2." Later, he gives a table showing good correspondence between values of A calculated, and values observed.

These observations could be more valuable if the quantity A, termed "the photographic effect," were more precisely defined. It can only be presumed, in view of reference to their paper, that it refers to percentage number of grains made developable in a one-grain layer plate of grains of approximately equal size, and, as assumed by Slade and Higson "identical quality." Since no statement as to this or other such effect is made, we cannot feel that this places Slade and Higson's formula beyond criticism; it does not seem to us compatible with Toy's own independent results, of the variable sensitivity of grains of the same emulsion, of the same shape and size. Neither a variable chance distribution of sensitizing nuclei, nor a quantum hypothesis of exposure gives such a relation, so that it remains in conflict with both types of hypothesis discussed here.

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[18] *P. J.*, **62**, 89 (1922), "The Action of Soluble Iodides and Cyanides on the Photographic Emulsion," S. E. Sheppard.

[19] F. C. Toy: *Proc. Roy. Soc.*, A, **100**, 109 (1922).

[20] *Loc. cit.*, p. 110.

Under these conditions, an uncertainty cannot but be felt as to the conclusiveness of Toy's otherwise probable result "that over the spectral range used . . . radiations of different frequencies do not act independently in producing the photochemical change, but probably simply as a total amount irrespective of any difference of quality;" a result contrary to Slade and Higson's conclusion from their data that the same amount of energy as a monochromatic radiation has more photographic activity than as complex radiation such as "white light."

The existence of differential "sensitivity" amongst grains of the same size in one and the same emulsion was confirmed and extended to grains of the same geometrical shape by Toy.[21] Since his data did not extend below 30 per cent. developability, it is not profitable to compare the curve of *percentage* grains against *exposure* with Slade and Higson's results. It must suffice to point out again that this result does not seem to be compatible with the premises on which Slade and Higson found their formula.

II. TENTATIVE THEORY OF THE RELATION OF SENSITIVITY VARIATION TO THE CHARACERTISTIC CURVE.

The sensitometric characteristics of an emulsion are expressed in their entirety by the characteristic, or H. and D. curves, with the proviso, that the curves will possibly differ accordingly as an intensity or a time scale of exposures is impressed on the plate or film. If Schwarzschild's relations hold, they will differ only in the density ordinate by a common factor p and have the same form. The conclusions of Slade and Higson that intensity enters into the density-exposure function as I^2 for small values of I (and large values of t) and as I for large values of I (and small values of t) do not for the reasons cited appear to us conclusively proven.

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[21] F. C. Toy: *Phot. J.*, 61, 417 (1921).

Assuming, provisionally, that the incident energy is represented with sufficient accuracy either by It_c when t is constant, or by $I_c t$ when I is constant, then the sensitometric characteristics deducible from the curves are:

D_{max}	Maximum density developable
γ_∞	Maximum slope
i	Inertia if no regression occur
or a and b	Nietz's coefficients of the time-gamma convergence point
Lat.	Latitude
K	Velocity-constant of development

The empirical comparison of size-frequency curves with the characteristic curves and the derived values has only a limited value, however. It is desirable to have at least an orienting theory of the general relation of sensitivity-variation to the density-exposure function as a whole. We shall only assume at first that a statistical variation of sensitivity exists among the grains of the same emulsion, without prejudice as to its origin or explicit nature.

The conception of statistical variation among reacting units—*prima facie* of one chemical species—has not entered much into general chemical dynamics. Statistical variation of gas molecules as to velocity has been from the first, however, a feature of the kinetic theory of gases. Through statistical mechanics and radiation theory this has begun to react powerfully on the theory of chemical kinetics. While we may utilize conceptions developed in this field, notably by W. Mc. Lewis, R. C. Tolman and E. K. Rideal, it is in the field of biochemistry [22] that the application of variation to reaction velocity has been made most definite; this is most notable in regard to problems of the immuno-chemistry of cells and unicellular organisms. Biologically the existence of variation has to be admitted *de facto*, without, so far, any satisfactory theory of its origin prevailing.

Whether we are dealing with molecules, grains or cells as reacting units, variation of sensitivity (reactivity) amongst the units will greatly affect the course of the reaction, so that it may depend chiefly on this, and only secondarily upon the course of the fundamental reaction.

Now the actual progress of the reaction may be expressed graphically in two ways. First, as the usual accumulation or time curve, the amount changed being plotted as ordinate, against time as abscissa. For dispersed granules or cells, we could plot number x volume against time. There is also the rate curve, the ordinates being the amount of substance changed per unit time $\frac{\Delta x}{\Delta t'}$ plotted against time. The former is the more usual in reaction kinetics, while the latter is the "mortality curve" of vital statistics. The latter curve is evidently the first derivative of the time curve, and we can pass from the *rate* curve to the *time* curve, either empirically by graphic integration, or algebraically, if the differential equation expressing the rate curve is known and integrable. Conversely we can obtain the rate curve from the time curve by differentiation.

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[22] Cf. S. C. Brookes: *J. Gen. Physiolog.*, I, 61 (1918).

Essential to the present argument is the fact that under certain conditions the *rate* (or mortality) curve may be identical with the variation (or frequency) curve of individual resistivities (inertias, reciprocals of sensitivities). Supposing the time curve replaced photographically by an exposure curve

$$D = f(E),$$

then with certain restrictions to be discussed, the first derivative of this

$$\frac{dD}{dE} = f'(E)$$

would give the variation curve of inertias of the reacting particles, or correlatively, the sensitivity-frequency curve.

The importance of the first derivative of the characteristic curve was first noticed by Nutting, Jones and Mees [23] for positive emulsions. It was introduced as dependent upon finite groups of grain sensitivities by Ross [24] in a theoretical discussion of the density-exposure function, and attention was a little later drawn to the subject in respect of negative emulsions by F. F. Renwick.[25] The latter's statement of the fundamental property of the derived curve appears to agree to a large extent with the conclusions reached here. "Since every ordinate of the derived curve represents the amount of silver bromide which has just attained the developable condition at the corresponding exposure, it is evident that we might regard each ordinate as a measure of the quantity of silver bromide in the film having that particular true inertia value." It is now evident that if for "quantity" we substitute "number of particles per unit area" that the first derivative becomes the statistical frequency curve of inertias—provided there is no reduction of intensity through the film, as noted by Renwick, but also provided that the relation of grain size to grain sensitiveness is explicit.

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[23] *P. J.*, 54, 342 (1914).

[24] *J. Opt. Soc. Amer.*, 4, 255 (1920).

[25] *P. J.*, 61, 10 (1921).

Considerable modifications are necessary before these premises can be applied to actual sensitometric curves—obtained normally as

$$D = \phi\ (\mathrm{Log}\ E),$$

with first derivative

$$\frac{d\,D}{d\,(\mathrm{Log}\ E)} = \phi'\ (\mathrm{Log}\ E).$$

To facilitate this application we have developed an approximate theory of the density-exposure function for very restricted conditions. The direct theoretical development of a function for the characteristic curve is beset with difficulty. Application of the calculus to a system composed of finite discontinuous units, such as silver halide grains, is itself contestable, and the difficulty becomes greater if statistical variation of the grain-sensitivities is admitted. The following device has been adopted for an indirect attack. A relatively simple photochemical reaction is assumed in an ideal homogeneous system. In the reaction equation obtained, the heterogeneity or variation factor is then introduced by replacing the reaction-constant of the function first obtained by various sensitivity or inertia variations.

The formula developed for photochemical change in a homogeneous layer is based on the Grotthus-Draper law that the rate of change is proportional to the energy absorbed by unchanged photolyte. The fundamental premise is therefore the same as that of Hurter and Driffield; no account is taken, however, of the absorption by altered silver halide for reasons discussed in a fuller paper. The expression obtained, for the general case of moderate absorption is:

$$e^{-K\delta x} = e^{-K\delta a} + (1 - e^{-K\delta a} e^{-KkI_o t}). \qquad (1)^{26}$$

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[26] Deduction of this expression is dealt with in a fuller paper on this phase of the subject. J. Plotnikoff's integration (*Zeit. wissent. Phot.*, 19, 238 (1920)) of a similar differential equation leads to a different result and appears to us incorrect.

Where k = coefficient of absorption of supposed monochromatic radiation
δ = thickness of layer
a = original concentration of photolyte per unit volume
x = amount of photoproduct per unit volume

Before applying any considerations dealing with the heterogeneity of the actual system considered, we may note that this expression reduces to two much simpler forms:

(*a*) When the absorption factor $k\delta$ is very large:

Equation 1 may be written

$$ln \frac{[e^{K\delta x} - e^{-K\delta(a-x)}]}{[1 - e^{-K\delta(a-x)}]} = KkI_\circ t \qquad (2)$$

which, if $e^{-k\delta}$, approaches 0, becomes

$$ln\,(e^{K\delta x}) = KkI_\circ t$$

whence

$$\delta x = kI_\circ t \qquad (3)$$

a linear relation between amount of photoproduct and exposure.

(*b*) When the absorption factor $k\delta$ is very small, functions of the type $e^{-K\delta(\ \ )}$ can be expanded and reduced to:

$$e^{-K\delta(\ \ )} = 1 - K\delta(\ \ )$$

so that we have from equation 2

$$ln \frac{K\delta a}{K\delta\,(a - x)} = ln \frac{a}{a - x} = KkI_\circ t$$

$$x = a(1 - e^{K'I_\circ t})\,. \qquad (4)$$

This equation is of the so-called monomolecular form as found for the "dark reactions" and proposed by Elder for the density-exposure function. Its insufficiency *per se* for representation of this function has been exposed by Ross. According to present considerations, it could only be valid for a homogeneous material with very low absorption. The course of the reaction in such a homogeneous system may tend to approach either the linear form (equa. 3), when absorption is high (*e. g.*, the maximum of the wave-length sensitiveness curve) or the logarithmic form, when absorption is low (*e.g.*, the limits of the wave-length sensitiveness curve). But, in any case, photographic emulsions are heterogeneous systems.

Effect of Heterogeneity of Material.

We do not propose at this stage to consider the effect of modifying assumptions proper to the homogeneous reaction, *e.g.,* allowing for absorption by the altered silver halide, for limited autocatalysis by the photoproduct, etc.[27] It has appeared to us more important to proceed to consideration of sensitivity variation.

Consider the simplest case of sensitivity distribution, *viz.,* negligible deviation from a certain average value. The sensitivity-variation curve, corresponding to the rate curve, would be a straight line perpendicular to the abscissa. Its integral, the time curve, would, if the fundamental reaction is supposed uniform (of zero order), follow the axis to this point of intersection, then rise perpendicularly. That is, all grains would become developable at the same exposure, whatever the photochemical law for the single grain.

Apart from inherent and "quantum" sensitivity variations, in thick layers absorption of light in the upper layers involves an apparent gradient of sensitivity through the film. This is partly allowed for in the deduction of a reaction formula, which remains, however, of complicated form except for very high or very low values of the absorption factor. (See previous section.)

Following Ross, we may combine this absorption factor with inherent variation of sensitivity. Before resorting to this artifice it will be simpler to limit consideration at first to one-grain layers.

Suppose the photochemical absorption proper to be of such large or such small magnitude as to give the limiting cases obtained for the ideal reaction:

a. $x = kE$ Uniform rate

b. $x = a(1 - e^{-kE})$ Monomolecular rate

Then let us assume that the material is broken up into "microsystems," each obeying one or other of the above formulæ, but in either case having different individual values of k—the velocity constant—distributed according to some probability function, *e.g.,* the normal law of error. In either case, if k does not vary, all "grains" would become developable at the same exposure. We must then equate the actual rate to the distribution function of the k's—the sensitivity distribution. For immediate convenience in testing the "size variation" hypothesis of sensitivity, we have selected distribution functions of type found experimentally to represent our actual size-frequency data. The general progressive increase of "speed" with grain size shown in our data (p. 514) warrants such an attempt.

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[27] The changes in developability of the grain, with different developers, with solarization, with iodide, etc., are not consistent with so simple a view as that adopted, but these are secondary properties. The evidence from Slade and Higson's data (see p. 492), shows, however, that the possibility of autocatalysis being a primary factor requires further consideration.

In general, if the granular material does not cover the whole of a given area, say 1 sq. cm., for which the reaction is being considered, the available exposure will be that falling on the normal grain surface or projective area, S, *i.e.*, according to previous considerations.

a. $$\frac{dx}{dt} = kI.S; \quad x = kS.E$$

b. $$\frac{dx}{dt} k'I.S(a-x); \quad x = a(1 - e^{-k'SE})$$

provided the grains have the same sensitivities (or inertias), and $S = \sum_{o}^{n} s$, the sum of areas of n grains per sq. cm. Now we may obviously have two extreme cases for the function $k = f(i)$, the variation of inertia, in relation to size of grain. These are:

Case I.—$k = f(i)$, totally independent of grain size. Then, if the grains are the *same size*, integration has to be extended only to inertias, if of different sizes, to both inertias and grain sizes.

Case II.—$k = f(i)$ is a function of grain size. For example, the sensitivity may vary directly as the grain size, or the inertia be inversely proportional thereto. This is the simplest possibility, integration over a range of sizes being at the same time integration over sensitivities.

According to the argument developed, either of these cases may be conjoined with the fundamental "molecular" equations a or b. This procedure is developed, to illustrate the modifications, in the following synopsis:

EQUATION TYPE A.

	Fundamental reaction.	Variation function of inertias.	Size Condition.	Integral, or Exposure function.
	$\frac{dx}{dE} = k$	$k = y = y_0$	All same size	
I.	$\frac{dD}{dE} = k$	$f(i) = y = y_0$	S	$D = kEB\,s$
II.	$\frac{dx}{dE} = k$	$k \quad f(i)$	S	$D = s\int f(i)\,di$
		e.g., $f(i) = Be^{-ki}$	S	$D = Bs\int e^{-ki}di$
				$= Bs\int e^{-kE}dE$
				$= \frac{D_m}{k}\left(1 - e^{-kE}\right)$

NOTE.—A uniform rate of reaction, combined with an exponential inertia-distribution, gives the same type of density function (for constant grain size) as the "monomolecular" rate combined with uniform inertia-distribution. If the size of grain s varies, integration must be extended over $f(s)ds$ for the corresponding limits as $f(i)di$—which are not given unless the relation of i to s is explicit.

EQUATION TYPE B.

	Fundamental reaction.	Variation function of inertias.	Size Condition.	Integral, or Exposure function.
I.	$\frac{dx}{dE} = k(a - x)$	k constant	S same size	$D = D_m(1 - e^{-k'E})$
II.	$\frac{dD}{dE} = k'(D_m - D)$			
	$\frac{dD}{(D_m - D)} = k'\,dE$	$k' = f(i)$ $k'\,dE = f(i)\,di$	S	$\int\frac{dD}{D_m - D} = \int f(i)\,di$
				$\frac{1}{D_m}\, l_n \frac{D_m}{D_m - D} = (1 - e^{-ki})$
				$\frac{D_m}{D_m - D} = e^{\frac{D_m}{k'}(1 - e^{-k'E})}$
				$D = D_m(1 - e^{-u})$

NOTE.—This expression, $D = D_m(1 - e^{-u})$ which may be written

$$D = D_m\left[1 - e^{-D_m\int_0^E e^{-k'E}dE}\right]$$

has considerable similarity to that obtained by Ross (*J. Opt. Soc. Amer.*, 4, 255 (1920)), *viz.*,

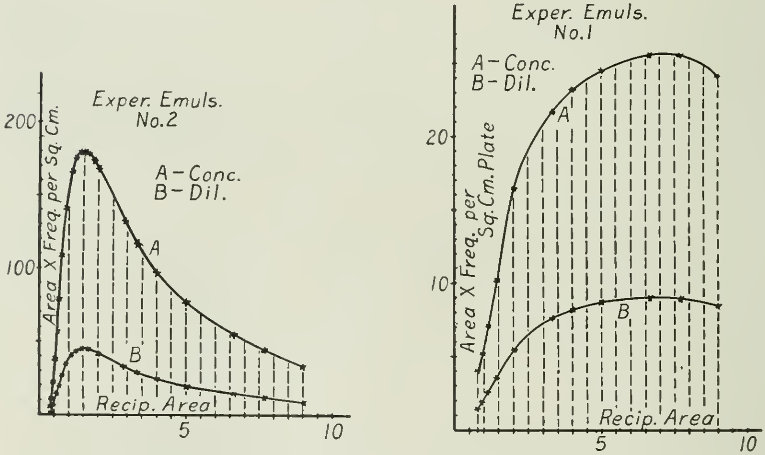
$$D = D_m \left[1 - \frac{1}{n} \sum_{p=0}^{p=n-1} e^{-kr^p E} \right]$$

where n is the finite number of classes of grains of different sensitivities supposed arranged in geometrical progression, p the sensitivity factor, r the ratio of sensitivities of different groups.

Relation of Size of Grain to Inertia.

On the " quantum " theory, as developed by Dr. L. Silberstein, the relation of " size of grain " to " inertia of grain " is apparently quite explicit. The projective-area of the grain, say s, is the measure of its chance of being hit by a quantum, hence, is the effective sensitiveness, statistically. On the other hand, the " size of grain " considered in this is not necessarily the " size " as found by the direct measurements of frequency, nor is the distribution function of sizes thus found directly available for the quantum theory, but requires some corrections for reasons noted later. We may, without immediate recourse to this theory, test empirically the hypothesis that the effective sensitivity of a grain is its " size "—to a first approximation, its " area." Then, the value of $f(i)$ in the foregoing synopses will be given by the distribution of *reciprocals* of the areas of the grains. On this

Fig. 4.

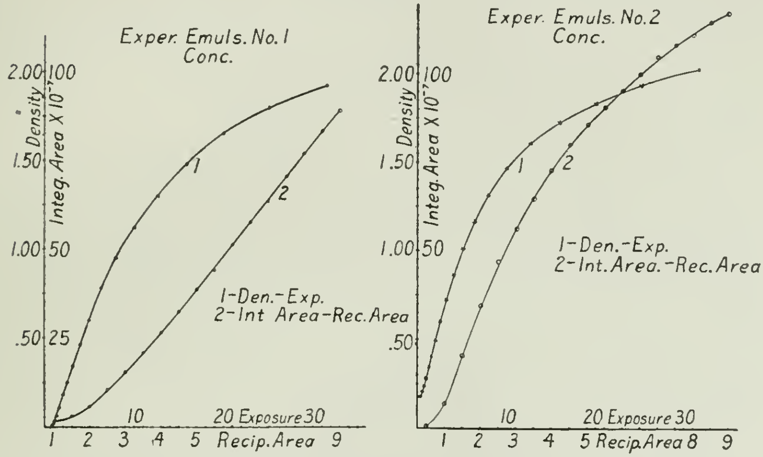


assumption, the relation of size of grain to inertia is explicit; if the reciprocal area-frequency (= inertia-frequency) per sq. cm. of plate be multiplied at each point by the area itself, the resultant curve should give, to a first approximation, the first derivative of the density-exposure function, when expressed in suitable units. Such curves are given in Fig. 1, as constructed from the original " frequency curve " for the two types of emulsion in question. They are each plotted for two cases,

A. For the total thickness of original plates;

B. For a one-grain layer.

FIG. 5.

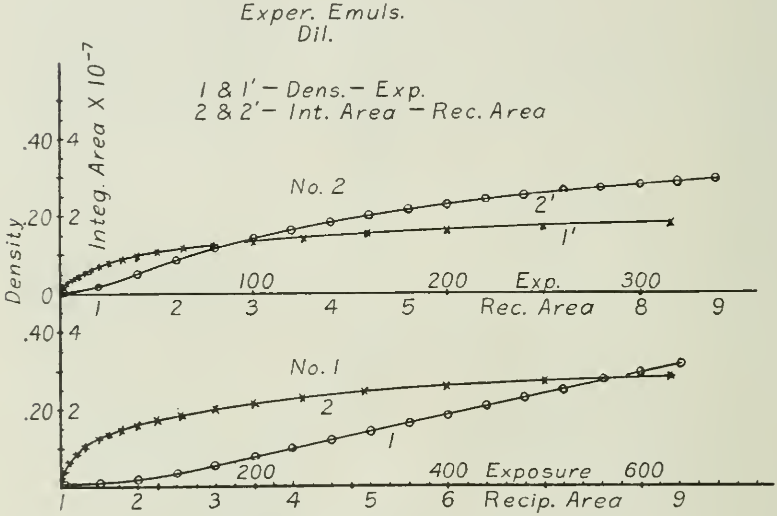


If now the curve No. 1, A and B, and No. 2, A and B (Fig. 4), are integrated graphically, the resulting curves should be comparable with the D-E curves. This has been done for both concentrated and dilute experimental emulsions and the results are shown in Figs. 5 and 6. It is obvious that for adequate comparison both abscissæ and ordinates should be expressed in the same units in both cases. The scale for the exposures is obtained from the condition that the maximum density must be reached with exhaustion of all classes of grains. For the density ordinates, the values 2 and 2′ in Figs. 5 and 6 should be multiplied by a factor for conversion of silver halide of a given grain to density, at same gamma as in Figs. 11 and 12. This correction will be applied when present work on the photometric constant is completed.

It will be seen that the "synthetic" curves give a "cut," as found by Renwick, but a very prolonged under-exposed region, and do not show very satisfactory correspondence with the actual sensitometric curves. The very prolonged "under-exposed" effect corresponds, however, to the fact that no allowance has been made for reduction of available light energy in the thickness of the film. With this correction it appears possible that the comparison may be improved.

Ideally, it would seem that the one-grain layer would be the most satisfactory for comparison. The difficulty lies in the measurement of very small "densities"—of the order .002 to .20, with sufficient precision. Work on this is in progress, and a more satisfactory comparison will then be possible.

FIG. 6.



Experimental Data in Size-Frequency.

To determine size-frequency of grains in large amounts of emulsions we have developed methods of sedimentation and centrifugal fractionation.

For small amounts of emulsion, such as may conveniently be removed from a coated plate or film, we have developed a direct micrometric method. A "one-grain" layer of convenient distribution is produced. Then by means of a high-power microscope, the particles are either photographed, or their outline drawn with a camera lucida. This stage is further enlarged by projection to a total of some 10,000 diameters, and the areas measured directly. For grains sufficiently circular, this is done by measurement of diameters, while larger polygonal grains are planimetered. The data are classified, and the size-frequency curves plotted. Eleven emulsions have already been analyzed in this way. They are enumerated below in Tables I and II.

Most of Table I is self-explanatory; the columns y_0, k and α have the following significance: It is found that the size-frequency curves of all emulsions can be represented by probability equations of two types:

$$\text{Exponential } f(s) = y = y_0 e^{-ks} \tag{5}$$

$$\text{Gaussian (modified) } f(s) = y = y_0 e^{-k(s-a)^2} \tag{6}$$

and the values given refer to the parameters of the corresponding equations.

It is worth noting here that previous estimates of the thickness of the grains of the silver halide in photographic emulsions have been in many cases too low. If, from the weight of silver halide and the number of grains per sq. cm. of plate, we determine the equivalent volume of the average particle, assuming the density to be that of pure silver bromide (the error in doing this is not greater than 3 or 4 per cent. even with fairly large amounts of iodide present), it is then easy to get the approximate thickness of the average grain (1) where the grains are spherical by determining their diameter

$$d = \sqrt[3]{\frac{6V}{\pi}}$$

and (2) where they are flat by dividing the average volume by the average projective area.

In two of the process emulsions studied which have almost entirely spherical grains this calculated diameter corresponds very closely to the average diameter determined statistically by the microscopic method. The third process emulsion (Process C), which is seen by examination of the photomicrographs to have a number of angular grains (usually indicating flatness) has a cal-

TABLE I.

Grain Characteristics—Average Size Grain.

Type of Film or Plate.	No. Grains per sq. cm. =N.	Gms. Ag-halide per sq. cm. of film of plate.	Per cent. Conc. Ag-halide per sq. cm. Emul. on plate or film.	Equiv. Diam. in μ.	Projective Area in μ^2.	Equiv. Vol. in μ^3.	Wt. in Gms. x 10^{12}.	Thickness in μ.	Ratio Thick:Diam.	Max. Grain Size Obs. in μ^2=M.	y_0	k	a
Process A.... (Lantern Slide)	4.30 x 10^9	0.000840	31.4	0.383	0.115	0.0301	0.195	0.386†	1: 1	1.2	4000.0	5.81	
Process B....	0.668 x 10^9	0.001366	33.6	0.844	0.560	0.317	2.05	0.846†	1: 1	1.6	340.4	8.95	0.555
Process C*...	3.08 x 10^9	0.001422	35.4	0.874	0.60	0.0711	0.46	0.710†	1: 1.2	3.2	286.7	4.72	0.630
Positive Emulsion....	1.853 x 10^9	0.000870	36.8	0.704	0.389	0.0726	0.47	0.187	1: 3.8	2.2	573.5	2.52	
Medium Speed A...	2.11 x 10^9	0.001213	33.4	0.757	0.450	0.0889	0.575	0.198	1: 3.8	6.2	1068.0	2.98	
Medium Speed B...	0.941 x 10^9	0.001300	32.5	0.799	0.502	0.213	1.38	0.124	1: 1.9	6.2	276.9	4.27	0.533
Medium Speed C...	1.50 x 10^9	0.001677	33.9	1.41	1.567	0.173	1.12	0.110	1:12.8	8.4	221.6 32.2	4.27 12.20	0.790 1.860
High Speed A...	0.656 x 10^9	0.001350	37.1	0.966	0.732	0.318	2.06	0.435	1: 2.2	8.6	110.2 310.9	0.953 3.36	
High Speed B...	0.478 x 10^9	0.001470	33.7	1.67	2.198	0.467	3.08	0.216	1: 7.7	12.6	200.0 30.3	2.78 6.45	0.758 2.046
Experimental Emulsion No. 1	5.690 x 10^9			0.	0.167					1.4	2375.3	4.75	
Experimental Emulsion No. 2	1.660 x 10^9			0.	0.710					2.8	235.2	3.06	0.575

*This is a panchromatic emulsion.
†Volumes assumed to be spherical.

TABLE II.

Sensitometric Characteristics.

Type of Film or Plate.	K	$\gamma\infty$	Approx. $D_{max.}$	a	b	Relative H. & D. Speed.			Latitude.		
						1 min.	3 min.	10 min.	1 min.	3 min.	10 min.
Process A (Lantern Slide)	0.354	4.05	7.5	0 to 0.05	0 to -0.27	6	6	7	7	9	3
Process B	0.429	4.95	6.2	$\bar{1}.90$	-0.35	6	7	8	2.3	3.6	2.0
Process C*	0.262	4.87	7.3	$\bar{2}.91$ to $\bar{1}.05$	-0.25 to -0.31	27	47	76	9	3.0	3.0
Positive Emulsion	0.384	4.82	5.1	$\bar{1}.82$ to $\bar{1}.92$	0 to -0.18	8	9	10	4	7	3.2
Medium Speed A	0.398	1.39	5.5	$\bar{3}.63$	-0.32	366	729	918	316	316	316
Medium Speed B	0.352	1.23	4.2	$\bar{3}.78$	-0.15	439	763	856	282	200	200
Medium Speed C	0.323	1.62	5.7	$\bar{2}.00$	0	680	680	680	251	100	45
High Speed A	0.421	1.09	5.2	$\bar{3}.58$ to $\bar{3}.82$	-0.03 to -0.06	1236	1488	1560	178	159	71
High Speed B	0.321	0.932	3.7	$\bar{3}.15$	-0.05	2585	3820	4278	2510	794	398
Experimental Emulsion No. 1	0.254	2.42									
Experimental Emulsion No. 2	0.152	2.81									

* This is a panchromatic emulsion.

culated equivalent diameter somewhat smaller than the average projective diameter. For all the medium and high-speed emulsions the calculations were made assuming the grains to be flat. The ratios of thickness to projective diameter are given in Table I.

FIG. 7.

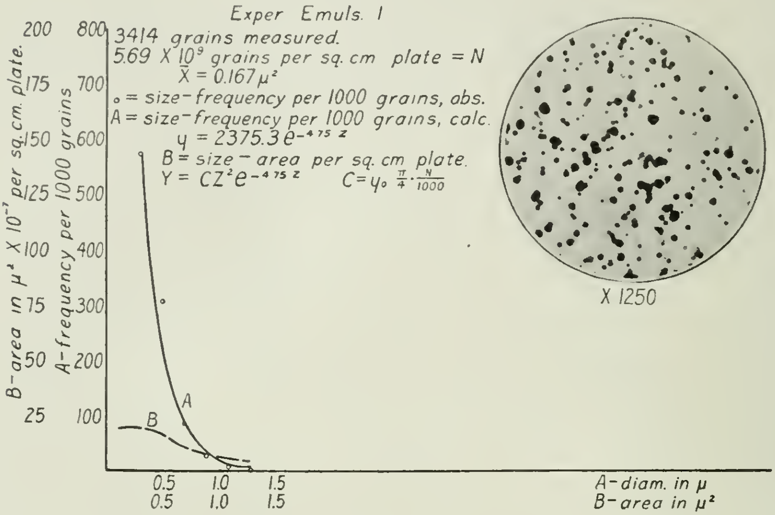
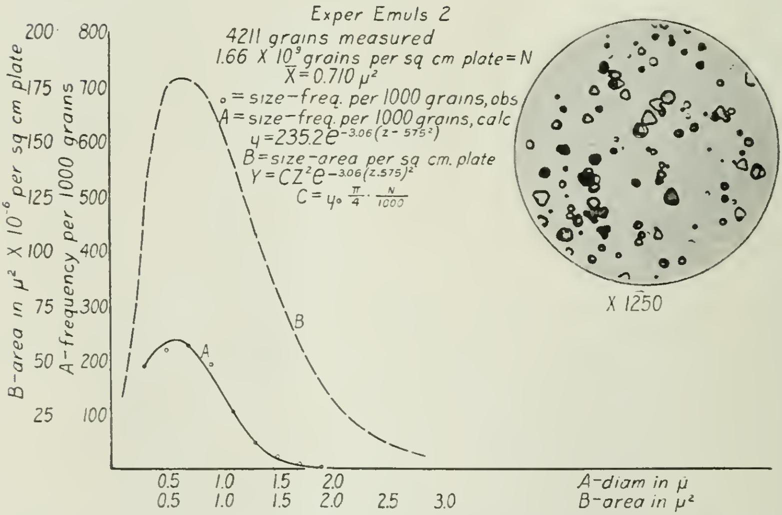


FIG. 8.



Experimental Data on the Sensitometry.

The characteristic curves for the emulsions examined were determined in two ways:

FIG. 9.

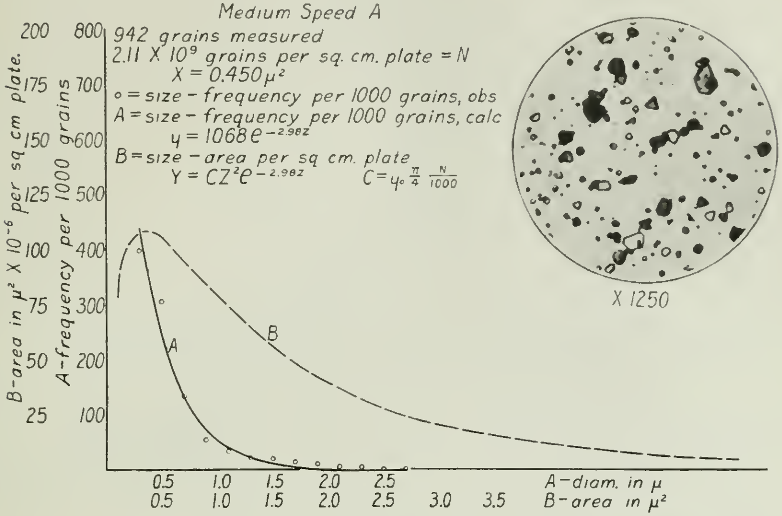
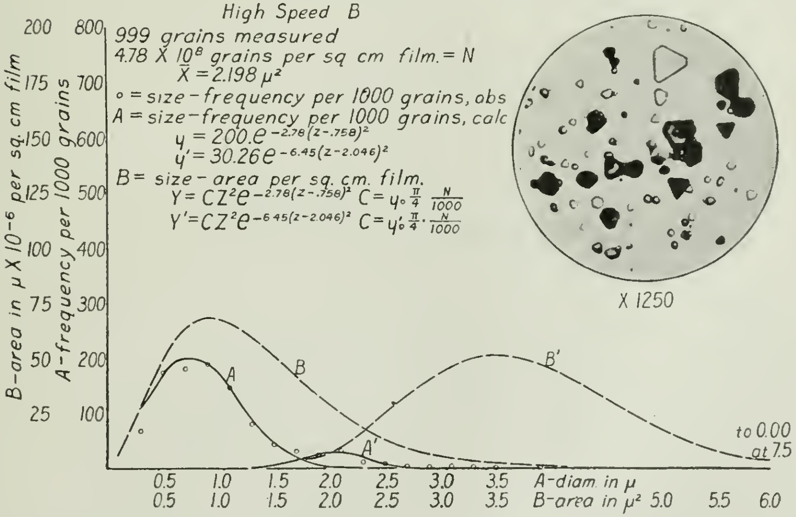


FIG. 10.

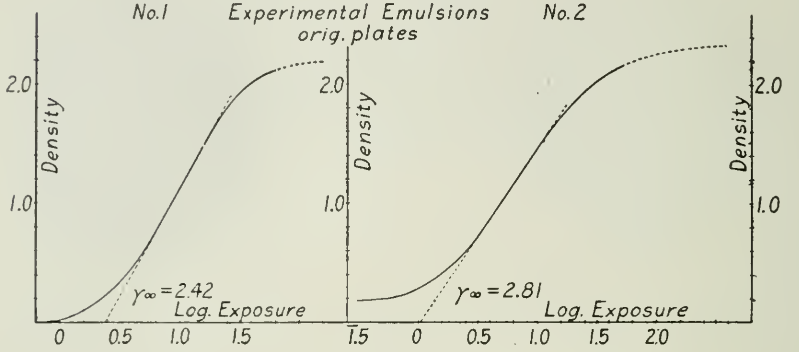


1. By intensity scales, using a Goldberg wedge and Higson's modification of Luther's crossed-wedge method. Curves for each

time of development were assembled, and the "family of curves" taken as giving the sensitometric data. (See Figs. 13 and 14.)

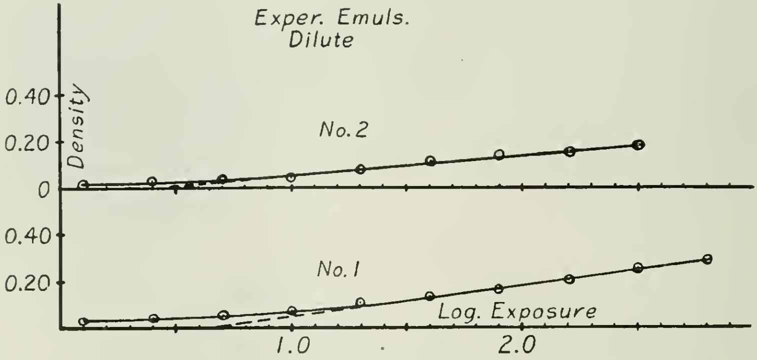
2. By time scale, using a Jones non-intermittent sensitometer, measuring the densities, and plotting the curves. (See Figs. 11 and 12.)

FIG. 11.



The sensitometric curves reproduced correspond to the frequency curves illustrated in Figs. 7, 8, 9, and 10.

FIG. 12.



III. NATURE OF SENSITIVITY AND RELATION TO GRAIN SIZE.

The data summarized in the second section of this paper show, as between different emulsions (mostly of the same fundamental type), a steady progression of "speed" with grain size. This progression becomes more evident if the relative "speeds" are tabulated against maximum grain sizes.

FIG. 13.

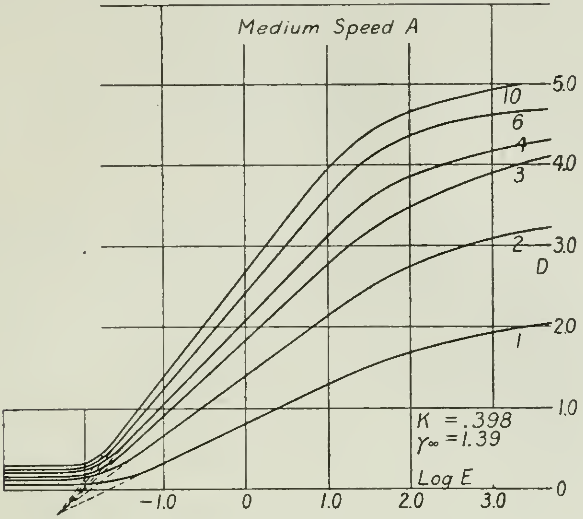
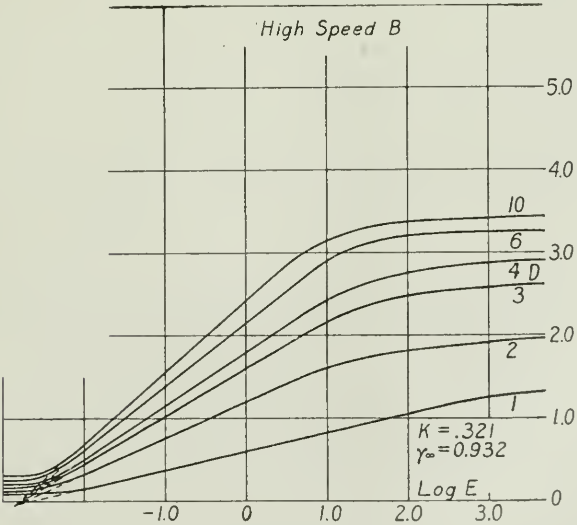


FIG. 14.



Since "speed" is obtained from a characteristic curve integrating the effects of grains of various sizes and sensitivities, in several layers, we cannot, from this, obtain any idea of the quantitative relation of size to sensitivity. The hypothesis was used in the foregoing section, that the *inertia* of a grain was inversely as its projective area, that is, its probability of development directly as its area, to deduce the density-exposure curve. The lack of agreement with the measured curves cannot be taken at present as refuting this hypothesis, for reasons explained. A more direct attack consists in determining microscopically the relation of developability to projective area for the same exposure in one-grain layers.[28] This has been done by A. P. H. Trivelli and F. L. Righter.[29] They extended their counts and area measurements to clumps of from one to as many as 33 grains; well-confirmed observations showing that with the type of emulsion used, and the technic followed in preparing the one-grain layers, if one grain of a clump was affected, the whole clump is developable.[30] The results, noted immediately, were in striking agreement with those calculated from a quantum theory of the exposure function proposed by Dr. L. Silberstein.[31] This formula he obtained, to a first approximation, as follows: Let the necessary and sufficient condition for a grain to become developable be absorption of at least one quantum of sufficient frequency, above a critical value, as known in photoelectricity. Consider equal-sized grains. Let there be N grains upon an area A and let S be the projective area of each divided by A, and let n– light-

TABLE III.

Emulsion.	Rel. Speed (Maximum).	Maximum grain area in μ^2.
Process A (lantern slide)	7	1.2
Process B	8	1.6
Positive	10	2.2
Medium Speed A	918	6.2
Medium Speed B	856	6.2
Medium Speed C	680	8.4
High Speed A	1560	8.6
High Speed B	4278	12.6

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[28] Cf. The. Svedberg and H. Anderson: *Zeit. wiss. Phot.*, 1920, p. 36; *Phot. J.*, 1921, p. 325.

[29] *Phil. Mag.*, 44, 252 (1922).

[30] Contrary to recent results of Svedberg.

[31] In the original paper a more rigorous deduction is given.

quanta impinge upon A—corrected for reflection, etc. To find q, the number of grains hit, the problem can be roughly treated as if N and q were continuous quantities.[31] At any stage the grains unaffected are $N-q$, the available fraction of area $S(N-q)$. Then for an increment dn of quanta

$$dq = S(N - q)dn$$

which gives

$$q = N(1 - e^{-nS}).$$

(It will be noted that this makes $\frac{dq}{dn}$, the "sensitivity," directly proportional to S, the projective area, as assumed in section II.)

This simple formula implies that the cross-section of a light-quantum is small compared with a grain. If it be further assumed that only full incidence of a light quantum[32] is effective, and let r be the average equivalent radius of a grain, such that $S=\pi r^2$ and let ρ be the radius of the light quantum. Then the effective area of the grain[33] will be

$$S^1 = \pi (r - \rho)^2 = S(1 - \frac{\rho}{r})^2$$

so that the formula becomes

$$\frac{q}{N} = (1 - e^{-\mu})$$

where

$$\mu = nS_1 = nS(1 - \frac{\rho}{r})^2$$

or if $\delta = \pi\rho^2$ be average area of cross-section of a quantum

$$\log(1 - \frac{q}{N}) = -nS\left[1 - \sqrt{\frac{\delta}{r}}\right]^2.$$

In Table IV the first column gives the number of grains in a clump, the second the average area s of a clump in square microns, the third the percentage of clumps affected out of all (N) clumps of each kind originally present, *i.e.*,

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[32] The effect of wave-length is discussed in Dr. Silberstein's original paper.

[33] It should be noted that if instead of the total projective areas of the grains as the targets for the light quanta, we assume that the effective targets are silver nuclei in the grains then the quantum hypothesis can still be applied, provided that the areas of the nuclei are distributed in a constant ratio to the total grain area. But, of course, the effective energy acting in a given time per square cm. of plate would be quite different in this case as compared with Dr. Silberstein's original assumption. Energy measurements are being made in this Laboratory which should help to clear up this point.

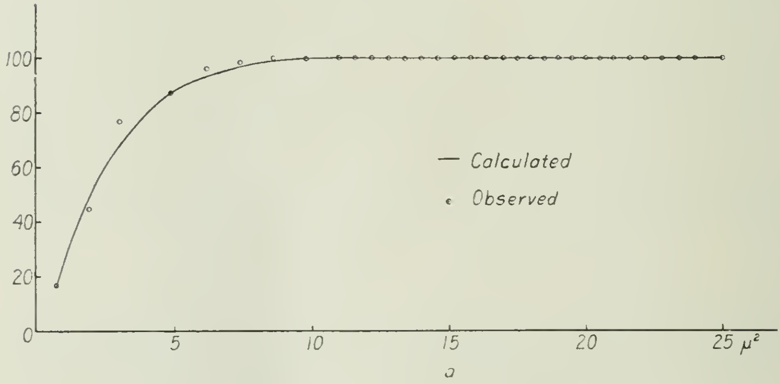
$$y = \frac{100\,q}{N}.$$

TABLE IV.

Clumps of	s in μ^2	y obs.	y calc.	Δy
1 grain	0.754	16.5	16.2	+ .03
2 "	1.925	44.9	48.4	— 3.5
3 "	2.03	76.6	68.9	+ 8.3
4 "	4.88	87.1	87.3	— 0.2
5 "	6.18	96.0	93.3	— 2.7
6 "	7.42	98.2	96.4	— 1.8
7 "	(8.6)	100.0	98.0	2.0
8 "	(9.8)	100.0	99.6	0.4
9 "	(11.0)	100.0	99.8	0.2
10–31 "	(12.0)	100.0	100.0	0.0
32 "	> 24.	100.0	100.0	0.0
33 "	> 25.	100.0	100.0	0.0

The data are represented graphically in Fig. 15.

FIG. 15.



As stated earlier, this theory makes "sensitivity" entirely a matter of "effective projective area," *i.e.*, area of grain not shielded by other grains, and probability of being hit by at least one light quantum. A recent paper by The. Svedberg,[34] which has appeared since the investigations noted here were concluded, requires discussion in this connection. Svedberg has followed up the observation by M. B. Hodgson, of this Laboratory,[35] that development starts at one or more points of a grain. By interrupting development of grains exposed in a one-grain layer, he was able to count the number of "nuclei" thus revealed per grain for a larger number of grains of two size-classes (diameter $> 1.18\mu$ and $< 1.18\mu$). "Assuming that the product of light action, *i.e.,* the substance of the latent image, consists of small centres distributed through the grain, or through the light-affected part of the grain according to the laws of chance," a certain grain will become developed if it contains one or more than one developable centre. Now according to the laws of chance the percentage probability for the occurrence of n centres in a grain is

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[34] *Phot. J.*, 1922, p. 186.

$$P_n = 100 . \frac{e^{-\nu}\nu^n}{n!}$$

where ν is the average number of centres per grain. Thus the percentage probability that the grain will contain at least one centre is $P = 100(1 - e^{-\nu})$.

Svedberg's results confirm this formula and thereby the hypothesis of a chance distribution of centres. Now it is apparent that this result is in good agreement with the quantum theory just discussed. It is, however, equally accounted for by the alternative hypothesis of a photocatalyst formed in emulsification, and located in the grains according to chance. As regards the relation to size of grain, Svedberg's data only confirm the rapid increase of sensitivity with grain size. They are insufficient in range to correlate the sensitivity factor ν absolutely with either volume or cross-section, although it is pointed out that the results obtained differ, so far as they go, for light and X-rays, a *volume* relation being indicated in the latter case. This result would be more probable on the emulsification-nucleus theory than on the quantum theory, and therefore confirmation is important. Trivelli and Righter's results[36] indicate that the proportion of developable grains in a one-grain layer increases more rapidly, with increasing area, than provided by the simple formula

$$q/N = 1 - e^{-nS}$$

where S is the projective area, and using nearly monochromatic blue light of $\lambda = 480\mu\mu$. This might be interpreted in terms of an increase in number of centres more nearly proportional to the *volume;* on Silberstein's quantum theory, as already noted, it is accounted for by allowing a finite cross-section to the quantum of dimensions comparable to the area of the grain.

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[35] J. FRANK. INST., 1917, p. 705, 184.

[36] *Loc. cit.*

If we term E, the exposure, provisionally $= It$, ν the average number of nuclei per grain (due to emulsification plus exposure), then evidently for a one-grain layer

$$q/N = 1 - e^{E\nu f(S)}.$$

Where $f(S)$ expresses the relation between ν and projective area of grain. If, on the simplest correlation discussed by Svedberg (and assumed provisionally by ourselves for "sensitivity," Sect. II) we put $f(S) = S$, we have

$$q/N = 1 - e^{-E\nu S}$$

which is of similar form to the simplest form of the quantum hypothesis

$$q/N = 1 - e^{-nS}.$$

The relations of these expressions to the density-exposure function are again of essentially similar type, initially. Silberstein[37] has pointed out that, assuming the simple formula above, for each class-size of an emulsion of type $\phi(S)$, where $\phi(S)$ is the equation of frequency distribution, the number of grains from s to $s + ds$ affected (at one quantum per grain) by n quanta will be $q_s ds$, where

$$q_s = \phi(S)\ [1 - e^{-nS}].$$

The total area of halide made developable will be found by integrating $q_s ds$ over the whole range of sizes, say from S_1 to S_2. Thus taking the exponential type of frequency curve $\phi(S) = Be^{-\mu s}$, from $S = S_1$ to S_2 where B and μ are constants, then the required integral or density value is

$$\Sigma = \frac{\beta}{(n-\mu)^2} \left\{ 1 + (n+\mu)S_1 e^{-(\mu+n)S_1} - [1 + (n+\mu)S_2] e^{-(\mu+n)S_2} \right\}$$

an equation which can be greatly simplified if $S_1 = 0$.

Formally, the same integration would apply to the equation derived from the "nucleus" hypothesis of Svedberg. It appears, however, that the actual range of "grain-areas" effective in the two cases would differ considerably. On the quantum hypothesis, for ordinary plates of several layers and high concentrations, the function $\phi(S)$ will not coincide with the size-frequency curve of that emulsion as determined by the methods discussed here. For, in the first place, if several grains form a contiguous clump, they may behave as *one grain* of class corresponding to their total projective area. Next, either a grain of a lower layer is shielded or not shielded.[38] If not shielded, it belongs to its proper class in one layer; if shielded it is reduced in class size to its unshielded portion. Hence, the effective size-frequency function $\phi(S)$ is not immediately determinable by mere counts, but has to be carefully corrected for the said factors. On the other hand, in the emulsification-nucleus hypothesis, the value S is the actually observed value in size-frequency determinations, and $\phi\ (S)$ the empirically determined size-frequency function. But, the correlation to n, that is, the exposure quantity (energy available or absorbed), requires in turn correction for diminution in passing through a multigrained layer. (See previous section II.) Hence it does not appear probable that a crucial distinction between the two hypotheses can be made on the ground of the integrated formulæ, since in either case mathematical refinements not immediately susceptible of experimental verification could be introduced making sufficient agreement with the actually measured density-exposure functions.

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[37] *Loc. cit.*

For physical optics, an experimental proof of the quantum hypothesis, of the discrete structure of light, is the issue. For photographic industry, if the " quantum " hypothesis is correct, the emulsion-maker has only to adjust the size-frequency curve of his precipitated silver halide, and ensure *absence* of inhibiting (desensitizing) substances in his gelatin to secure the maximum possible of speed, density, contrast, latitude, etc. If, however, the " emulsification-nucleus " hypothesis is correct, then the process of " sensitization " is of equal, or greater importance than that of grain-size determination; although at present apparently loosely coördinated with this, the possibility would exist of a more independent control of the two factors. In this connection, and as possibly helping to judge between the two hypotheses discussed, the phenomena of desensitizing are of great importance; particularly where it can be shown that the densensitizer has not been acting by mere destruction of the latent image as formed. In the subsequent paper certain independent evidence for the nucleus hypothesis will be considered, as also the problems of densitizing, nucleus activation, and what has been termed by Lüppo-Cramer [39] the topo-chemistry of the silver halide grain.

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[38] Cf. L. Silberstein, *loc. cit.*

SUMMARY.

1. The existence and nature of statistical variation of sensitivity among silver halide grains is discussed.

2. The relation of the statistical variation of sensitiveness, or inertia (its reciprocal), to the density exposure function is discussed. It is concluded that under certain conditions the first derivative of the density-exposure function will correspond with the intensity-variation function or curve.

3. The results of experimental determinations of grain-size-frequency curves are noted, and correlated with sensitometric data.

4. The decisive influence of the grain-size distribution and limits on the " speed " and other sensitometric variables is discussed in relation to the " quantum " and the " photocatalytic " theories of grain sensitiveness.

The Solvent Properties of Acetone. R. F. REMLER.—The paper takes up the following industrial consideration regarding acetone as a solvent: Uniformity of the present grade of acetone from calcium acetate, boiling point and volatility, freezing point, inflammability, dehydrating properties, miscibility with other solvents, use as a coupling or bending agent between immiscible solvents, relative test per gallon, physiologic effects and recovery. The solubilities of acetylene, cellulose acetate and cellulose nitrate, rosin and mineral oils, gums, resins, shellacs, animal and vegetable oils, fats and greases, waxes, asphalts, and bitumens, are discussed. Mention is also made of acetone in dry cleaning and leather industry, and as a constituent of paint, varnish, and carbon removers. (A. C. S. Abstract Service.)

Automatic Volumetric Analysis—Carbon Monoxide Recorder. HUGH S. TAYLOR and GUY B. TAYLOR.—An instrument for automatically making chemical analysis and recording the results is described. The instrument can be adapted to any case where two or more fluids can be mixed in regulated volumes, and the result of the obtained reaction of the fluids recorded by electrical conductivity, temperature rise, etc. Specifically the application of the apparatus to the analysis of flue-gas for carbon monoxide is described. (A. C. S. Abstract Service.)

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[39] *Loc. cit.*

THE STABILITY OF ATOM NUCLEI, THE SEPARATION OF ISOTOPES, AND THE WHOLE NUMBER RULE.*

BY

WILLIAM D. HARKINS, Ph.D.

Department of Chemistry, University of Chicago.

36. PERIODICITY OF TWO WITH RESPECT TO THE MEAN ISOTOPIC NUMBERS AND ATOMIC WEIGHTS.

THE periodicity of two which has been shown to appear in the atomic numbers, isotopic numbers, and abundance relations of the various atomic species, is found also in the mean values of the isotopic numbers, and therefore of the mean atomic weights when plotted against the atomic numbers. Figs. 8 and 10 show this periodicity particularly well. In the region of the light atoms up to atomic number 31 the isotopic number of an element of odd atomic number is in general one unit higher than when the atomic number is even. Strangely enough, among the elements of higher atomic number, practically all of the peaks which indicate a high isotopic number occur on atomic numbers which are even. Thus there is a reversal of the periodicity in this latter region. Up to atomic number 20 there is the sharp lower limit of 0 for the isotopic number, and this restrains the variation of this number to one direction. When the mean isotopic number rises sufficiently, it may vary in either direction, and in this latter case it is the even-numbered elements which have the higher isotopic numbers, and in a comparative sense, the higher atomic weights.

37. VARIABLES RELATED TO ATOM NUCLEI.

It has not been realized sufficiently that the variables used by the writer as the basis of his theory of nuclear structure and abundance, are all experimentally determined. In addition to the abundance (A) which has been used as the third dimension in the plots thus far given, there are five others which may be given in a two-dimensional diagram. These are the atomic weight (P), determined by both chemical and positive ray methods, and the atomic number, given both by the position of the element in the experimentally determined periodic classification of Mendelejeff, and by the X-ray method of Moseley. In addition to these there are the three variables—N or $(P-M)$, n or $(P-2M)$, and the ratio N/P, all of which are given in terms of the two experimentally determined variables, so they are themselves determined by experiment. As only two of these variables are independent, it is obvious that all of them may be represented in a single two-dimensional diagram, but since, in such a plot, only two of the variables are found to be at right angles with each other, it seems valuable to use rectangular axes for each pair of variables in order to make the relations as obvious as possible. In this way ten two-dimensional diagrams arise. Each of these may be supposed to represent a three-dimensional plot in which the third axis gives the abundance (A) of each atomic species.

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* Continued from page 356, vol. 194, September, 1922.

The ten diagrams are outlined in Table XXV.

TABLE XXV.

Outline of the Ten Two-dimensional Plots of the Variables P, M, N, n, and N/P, together with Equations representing Constant Values of the Variables.

(The ratio N/P is represented by R, and $(N/P)-0.5$ by R'.)

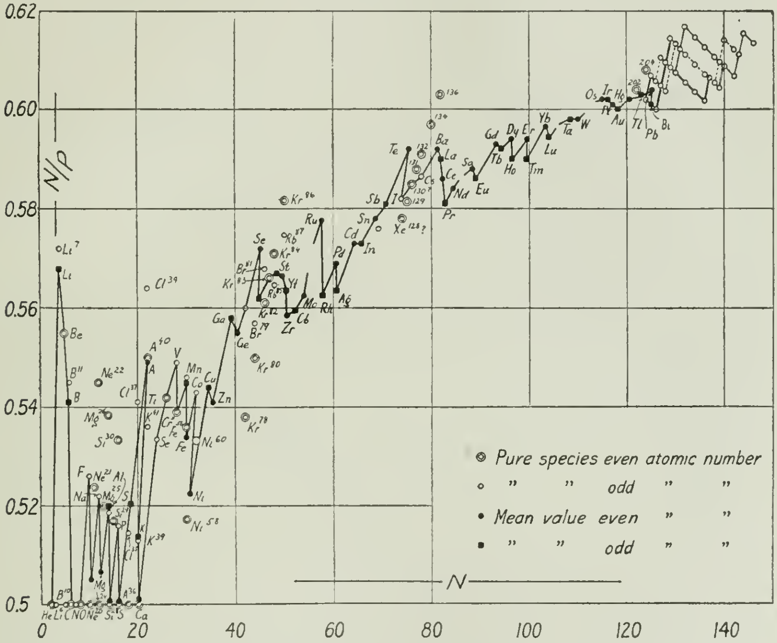
Figure.	Independent Variables	$R=k$. $R'=k'$.	$N=k$.	$P=k$.	$M=k$.	$n=k$.
5	P N	$N=PR$	$N=k$	$P=k$	$N=P-M$	$N=\frac{P+n}{2}$
6	M P	$P=\frac{2M}{1-2R'}$	$P=M+N$	$P=k$	$M=k$	$P=2M+n$
7	M N	$N=\frac{M(1+2R')}{1-2R'}$	$N=k$	$N=P-M$	$M=k$	$N=M+n$
10	M R'	$R'=k'$	$R'=\frac{N-M}{2(N+M)}$	$R'=\frac{P+2M}{2P}$	$M=k$	$R'=\frac{n}{2(n+2M)}$
8	P R'	$R'=k'$	$R'=\frac{2N-P}{2P}$	$P=k$	$R'=\frac{P-2M}{2P}$	$R'=\frac{n}{2P}$
15	N R'	$R'=k'$	$N=k$	$R'=\frac{N}{P}-0.5$	$R'=\frac{N-M}{2(N+M)}$	$R'=\frac{n}{2(2N-n)}$
16	n R'	$R'=k'$	$R'=\frac{n}{2(2N-n)}$	$R'=\frac{n}{2P}$	$R'=\frac{n}{3(2M+n)}$	$n=k$
9	M n	$n=\frac{4R'M}{1-2R'}$	$n=N-M$	$n=P-2M$	$M=k$	$n=k$
17	P n	$n=2PR'$	$n=2N-P$	$P=k$	$n=P-2M$	$n=k$
18	N n	$n=\frac{4R'N}{1+2R'}$	$N=k$	$n=2N-P$	$n=N-M$	$n=k$

Note.—All of the fifty lines for constant values in the ten figures are straight except eight, as can be seen from the equations.

The diagrams not already presented are given in Figs. 15, 16, 17, and 18.

Fig. 15, which gives the values of the relative negativeness (N/P) of atom nuclei plotted against the number of negative electrons (N) present, is very much like Fig. 8, which gives the same ratio plotted against the number of protons (P), except that in the former all of the peaks slope more toward the right.

FIG. 15.

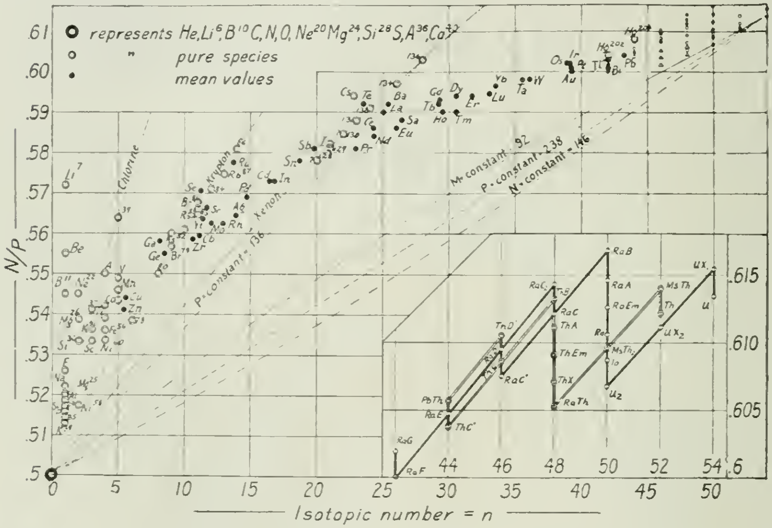


Figs. 17 and 18 are not very different in their form from Fig. 9 already given. The great similarity of the figures which relate any one variable to M, to P, and to N, is an illustration of the very simple relations which exist in a general way between these three variables.

Fig. 16 illustrates the increase of the relative negativeness (N/P) of the nuclei as the isotopic number increases. This plot has the interesting characteristic that all of the very abundant atomic species, with the exception of iron and aluminium, are represented by the *single point* at the origin. Thus 93 out of 100 of the atoms in the earth's crust are represented by this point.

The region of highest stability has very nearly the form of a parabola, and along any neutronal line ($n =$ const.) the stability decreases on passing vertically higher or lower out of this region. As an example, the lines showing the net nuclear charge as 92, the number of positive electrons as 238, and the number of negative electrons as 148, which are the values for ordinary uranium, are given. These lines indicate that for a nucleus with any of these three properties, represented by relatively large numbers, to exist, the isotopic number must increase to a sufficiently high

FIG. 16.



value (about 54) to cause the value of the relative negativeness to become sufficiently high (about 0.614) that the repulsion due to the large net positiveness may be thereby overcome.

The diagram in the lower right-hand corner of Fig. 7 indicates that during alpha disintegrations the isotopic number remains constant while the relative negativeness increases slightly. After several changes the nucleus becomes so negative in the relative sense that positively charged particles no longer leave it, but negative electrons are shot off. Each beta disintegration lowers the isotopic number by two, and in this region decreases the relative negativeness slightly more than two alpha disintegrations have increased it, as has been pointed out in an earlier section of the paper.

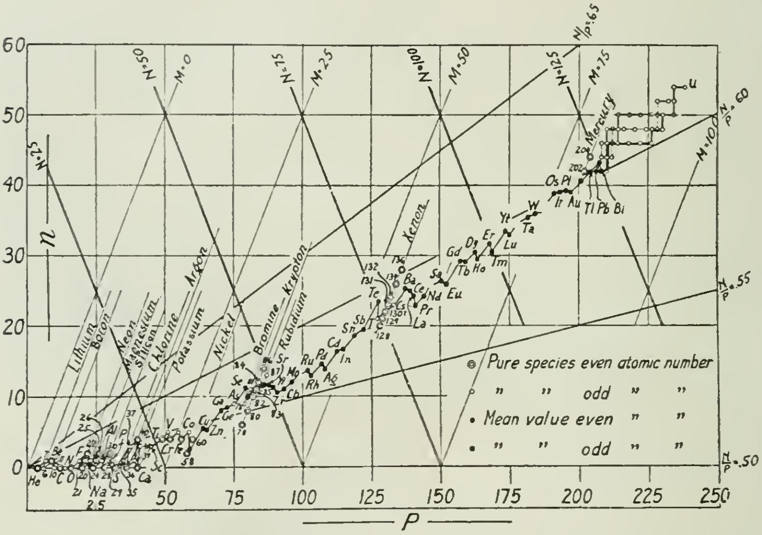
38. FUNDAMENTAL PRINCIPLES FOR THE PREDICTION OF ISOTOPES FROM THE CHEMICAL OR MEAN ATOMIC WEIGHTS.

A number of recent papers have made extensive predictions as to just what isotopes exist, but in every case all of these, except those made by the writer, have violated some of the fundamental relations of nuclear stability and abundance as presented in the earlier sections of the present paper, and so have not been justified by the later discoveries. Thus one writer predicted that all pure atomic species would be found to have atomic weights which are even numbers, and that fluorine, for example, would be found to be a mixture of isotopes of atomic weights 18 and 20, while another predicted that lithium would be found to consist of isotopes of atomic weights 5 and 7. The first of these predictions is at variance with one of the most important of the general atomic weight relations and did not need the findings of the positive ray method to show its falsity. The latter violates an even more general relation, but is more excusable, since the lithium nuclei are the simplest of all of the complex nuclei other than the basic alpha particle, so it might be *possible* that it would not follow the general relations, which indicate that the atomic weights should be 7 and 6, as predicted by the writer. Since the examples given above are only a small fraction of the erroneous predictions, it seems advisable to list below the most important general relations which seem to determine the existence or non-existence of atomic species.

Before doing this it seems advisable to call attention to the fact that the positive ray method, while it gives very remarkable results, should not be considered to be an infallible guide in determining just what isotopes exist, since at its present stage of development it will err in not finding those isotopes which exist in small percentages. Just what its limit of detection is, does not seem to be known, but it is probable that percentages equal to 1 or less per cent. are practically certain to be missed. It should also be kept in mind that the mathematical theory of the stability of a system so complicated as a complex nucleus is exceedingly involved, and that small changes in the number of nuclear electrons and protons may be expected to produce in some cases very great changes in stability, especially when the number of particles is small. Therefore all that can be expected of a theory is that it will point out correctly the general system, but it must not be expected that it will be able to give the details in every specific instance.

At the present time the greatest uncertainty which exists in this connection is that concerning the magnitude of the "packing effect" during the formation of more complex nuclei as compared with that which occurs in the formation of the helium atom from hydrogen. The approximate constancy of the packing effect as expressed by the *whole number rule* of Harkins and Wilson (1915) has already been discussed.

FIG. 17.



The principles to be kept in mind in the prediction of isotopes are:

1. A deviation of the atomic weight on the oxygen basis from a whole number which is more than two or three-hundredths of a unit greater than the experimental error, may be considered as a basis for the prediction of isotopes, particularly among the light atoms. The exact limits within which the atomic weight of a pure atomic species may vary from a whole number are still to be determined experimentally, but they are evidently very small.

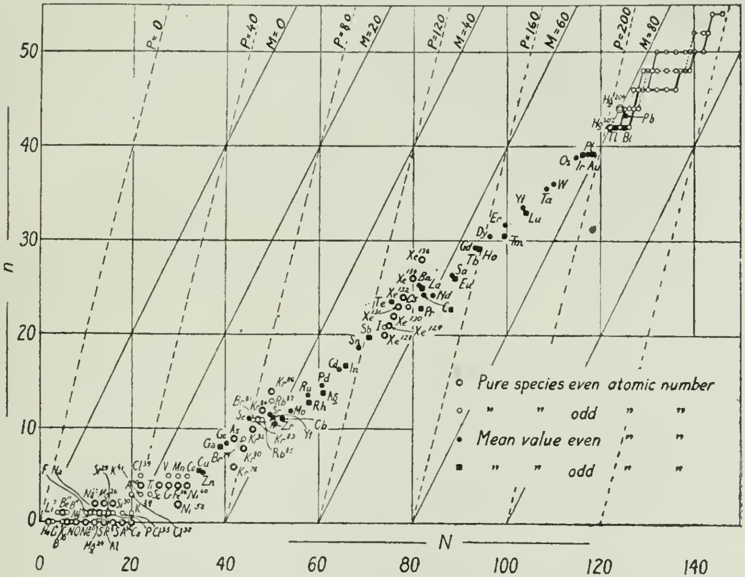
2. Among the light atoms an element may be considered, provided complicating factors are absent, to consist essentially of *one* atomic species if its atomic weight is the whole number given

by the more complete form of the Harkins-Wilson atomic-weight equation:

$$P = 2(M + f) + \tfrac{1}{2} + [(-1)^{M-1} \times \tfrac{1}{2}]$$

in which f is 0 up to atomic number 17, and is 2 between atomic numbers 22 and 27. On this basis helium, carbon, nitrogen, oxygen, fluorine, and sodium would be considered as single species. Also titanium, vanadium, chromium, and manganese are indicated by their atomic weights as nearly pure species in each case. While this relation alone might seem to indicate that beryllium of atomic weight 9, should consist of isotopes of atomic weights 8 and 10, the writer in 1915 considered that in this element a certain complicating factor is present, and that beryllium is a *single species* of atomic weight 9. This was found to be correct, for in 1921 G. P. Thomson discovered that beryllium is probably a simple element. The writer had concluded that the atomic-weight equation given above, developed on the basis of the idea that the principal isotope of a light element of even atomic number has a nucleus which is built of alpha particles alone, or these particles with two cementing electrons, could not be expected to apply

FIG. 18.



to beryllium. Thus while 3, 4, 5, 6, 7, 8, 9, or 10 alpha particles may hold together, it seemed probable that a third particle or group, aside from the two alpha particles in the beryllium nucleus, would be necessary to make a stable nuclear compound. From this viewpoint [37] it was assumed that the single atomic species had a nucleus of the formula a_2pe. Thus the beryllium nucleus may be considered to consist of two alpha particles and one neutron. The case of scandium will be treated in a later paragraph.

3. No isotope for which the value of N/P is less than ½, should be predicted. For example, as has been stated, one writer predicted that lithium would be found to consist of isotopes of atomic weights 7 and 5. Now the value of N/P for the latter of these two isotopes is 2/5, an entirely improbable value, since no species of complex atoms has as yet been found in which the value of this ratio is less than ½. Even the helium of mass 3, as found *experimentally* by Rutherford, in which this ratio seemed to be 1/3, has now been found to be fallacious and to actually be helium of mass 4, in which the ratio is ½.

4. The probability of the existence of a detectable quantity of an isotope is small if the value of N/P for the species is abnormally high for its particular value of M. Thus the atomic weight of lithium, as given by the Harkins-Wilson equation, is 7, which has proved to be the atomic weight of the isotope which constitutes about 94 per cent. of the element. The mean atomic weight, 6.94, indicates that there must be an isotope of lower atomic weight present. Now, according to principle 3 given above, the lowest possible atomic weight for this element of atomic number 3 is 6. On this basis the writer predicted that lithium would be found to consist of about 94 per cent. of an isotope of weight 7, with 6 per cent. of weight 6. The existence of these two isotopes was determined experimentally about a year later by G. P. Thomson and by Dempster. Rutherford had predicted the existence of isotopes of weights 6, 7, and 8. Now it may be possible that an isotope of weight 8 may exist, but the value of N/P for this atomic species is 0.625, which is higher than that for any known atomic species, and is entirely abnormal in the region of the light atoms, so it is not surprising that it was not revealed in the experiments.

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[37] *Proc. Nat. Acad. Science*, 2, 216–24 (1916); *J. Am. Chem. Soc.*, **39**, 856–60 (1917).

5. *Elements of Even Atomic Number.*—These should be divided into three classes: Light elements up to atomic number 26 or 28; heavy elements between atomic numbers 30 and 82, and radioactive elements of atomic numbers 82 to 92.

In all of these regions the most abundant isotopes will in general be those whose atomic weights are *even numbers,* and which at the same time have such values of N/P as give the highest abundance. Among the light atoms up to atomic number 16 the most abundant isotope has the isotopic number 0, between atomic numbers 18 and 30, with the exception of calcium (20), and nickel (28), it has the isotopic number 4. Thus in zinc the most abundant isotope has the isotopic number 4, and the abundance falls off as the isotopic number rises above this value. As the isotopic number of the most abundant isotope rises above 4, it may be expected that the isotopes will be distributed more evenly on both sides of the most abundant isotope, that is with both higher and lower isotopic numbers, but not with entire symmetry.

In general isotopes whose atomic weights are divisible by 4 will be more abundant than those divisible by 2 but not by 4, particularly in the region of the light atoms. As the atomic number increases this distinction may be expected to die out more and more.

Just what atomic species of even atomic number and odd atomic weight exist, it is difficult to predict, but they may be expected to be in general less abundant and less numerous than those of even atomic weight, and also in general to lie between the latter. *Thus in almost all of the cases thus far investigated isotopes of even atomic weight form the two extremes,* as 20 and 22 for neon, 24 and 26 for magnesium, 36 and 40 for argon, 40 and 44 for calcium, 58 and 60 for nickel, 64 and 70 for zinc, 78 and 86 for krypton, 116 and 124 for tin, 128 and 136 for xenon, etc.

In the region of the light elements there are not more than two isotopes of even atomic weight, but in the region of the heavy elements about 4 or 5 such isotopes may be expected. The total number of isotopes will be greater than this by the number of isotopes of odd atomic weight.

6. *Elements of Odd Atomic Number.*—While the relations for the isotopes of even atomic number are thus quite complex, *those for isotopes of odd atomic number are much more simple,*

not because the number of possibilities is less, but merely because the number of isotopes which are sufficiently abundant and stable to be apparent, is considerably less.

Thus the relations to be expected from the general theory *in the case of elements of odd atomic number* are: (1) Isotopes few in number in comparison with the elements of even atomic number; (2) isotopes mostly of odd atomic weight. In addition to this it is probable at least, so long as the atomic number does not become too high (which tends to level out contrasts of all sorts), that (3) members of the lithium series in general are more abundant than those of the meta-chlorine (beryllium) series.

In accordance with these principles it is to be expected, if the mean, or chemical, atomic weight is precisely known, and is very close to an odd whole number, that *the element consists of one pure atomic species,* or else mostly of one pure atomic species mixed with very small amounts of others. The most accurately known element weights of odd-numbered elements in the region of abundant isotopes (elements 28 to 81), are bromine, 79.92, iodine, 126.92, and silver, 107.88. Thus the mean atomic weight of bromine is 80 within the limits of error. If this were an odd number it would indicate the probability that bromine is wholly or almost wholly one pure atomic species. However, since it is an even number it indicates just as strongly that bromine is a mixture of two isotopes, 79 and 81 in atomic weight, and in nearly equal percentages. The atomic weight of iodine, on the other hand, is an odd number, 127, which indicates that it consists of only *one* atomic species.

"According to the above principles silver should consist either wholly or mainly of isotopes of atomic weights 107 and 109, rubidium of atomic weights 85 and 87, copper 63 and 65, and ruthenium of a single species mostly of weight 103, provided the chemical atomic weights are as precise as they are supposed to be. The general predictions are easily applied to the elements of even atomic number."

In accord with the prediction in regard to rubidium given in the last paragraph, as sent to the *Philosophical Magazine* in February, 1921, the isotopes of this element have been found by Aston to be two in number and to have the predicted atomic weights. The isotopes of lithium, atomic weights 6 and 7, were correctly predicted about a year before they were discovered, and those of boron, 10 and 11, several months before they were found.[38] In general the predictions have been verified in a remarkable way, especially since all of the *general* principles upon which they were based were published before any isotopes, other than those of neon and in the radioactive region, had been discovered. Thus three general predictions were verified by Dempster's discovery of the isotopes of zinc. These were:

1. That the region of abundant isotopes would begin at about atomic number 28. This prediction was made in 1915, and it was found in 1921 that zinc (at. no. = 30) is the first element in which the number of isotopes rises to 4.

2. That the number of isotopes would be large in this region for elements of even atomic number, not in general for those of odd number.

3. That the atomic weights would be even numbers in general for elements of even atomic number.

In December, 1920, Dempster reported to the Physical Society[39] that his preliminary results on the isotopes of zinc showed that their atomic weights were 63, 65, 67, and 69, and called the attention of the writer to the fact that these weights were not in accord with relation 3 listed above. The writer replied that he was confident that when the atomic weights were determined more accurately they would be found to be either 62, 64, 66, and 68, or else, more probably taking into consideration the probable N/P values in this region, 64, 66, 68, and 70. That the supposition was justified was proved by Dempster's more accurate final results, which proved to give the four numbers given last.

In a plot entitled "A General System of the Isotopes,"[40] drawn in December, 1921, the writer listed the most probable isotopes of the elements of odd atomic number, and what he believed would prove to be in general the most abundant isotopes of the elements of even atomic number—that is, those of even atomic weight. No attempt was made to predict those isotopes of even atomic number which have an odd atomic weight. The isotopes of tin listed were those of atomic weights 116, 118, 120, 122, and 124, and these were found later by Aston to be respectively third, second, first, seventh, and fourth in abundance among the isotopes of this element, and thus included *all* of the four most abundant isotopes. While tin has several isotopes of odd atomic weight they are relatively unimportant so far as abundance is concerned. Their atomic weights and relative abundance are: 117 (sixth), 119 (fifth), and 121 (eighth).

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[38] Harkins: *J. Am. Chem. Soc.*, 42 (1920), presented in April, 1920.

[39] Pages 147–8, Aston's "Isotopes" (1922).

[40] Fig. 21 of the present paper.

It is of interest that the most abundant isotope of zinc, of krypton, and of tin, all have atomic weights which are divisible by 4. Xenon, according to Aston's preliminary results, is exceptional in that its most abundant isotope has an odd atomic weight.

39. THE ALPHA PARTICLE AS THE MOST ABUNDANT ELECTRON GROUP, AND FURTHER EVIDENCE THAT ATOM NUCLEI ARE BUILT UP MOSTLY FROM ALPHA PARTICLES.

TABLE XXVI.*

Formulæ Expressing the Atomic Weight and Nuclear Positive Charge of the Light Atoms of Even Atomic Number.

(Most abundant isotope only.)

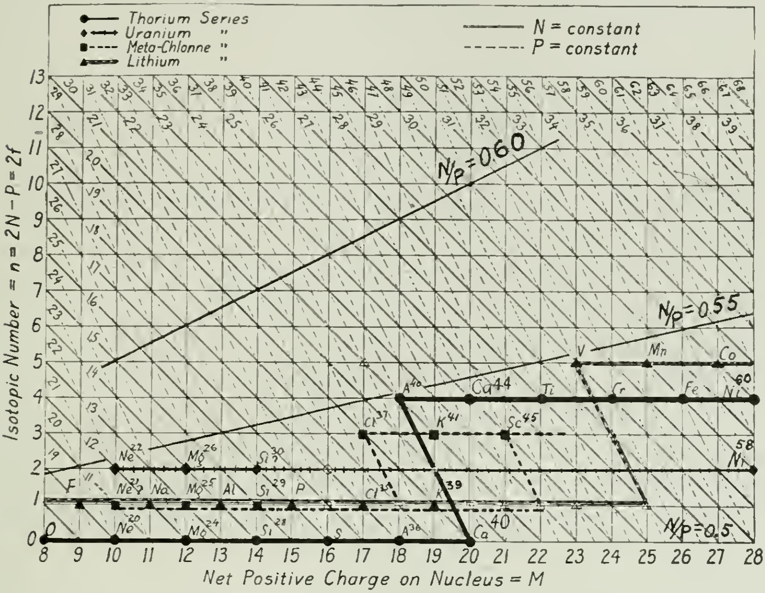
Atomic Number.	Element.	Nuclear Formula.	Atomic Number.	Element.	Nuclear Formula.
6	C	a_3	18	A	$a_{10}e_2$
8	O	a_4	22	Ti	$a_{12}e_2$
10	Ne	a_6	24	Cr	$a_{13}e_2$
12	Mg	a_6	26	Fe	$a_{14}e_2$
14	Si	a_7			
16	S	a_8			
18	(A)	(a_9)			
20	Ca	a_{10}			

* This table is similar to Table III, the difference being that Table III was prepared from the mean atomic weights before the discovery of the isotopes involved.

The first part of the present paper gave strong evidence from the standpoint of the *mean atomic weights* and the abundance of the elements (see particularly Tables III, IV, and XII) that all atom nuclei, other than that of hydrogen, are built up mostly from alpha particles. The present section will show that the atomic weights and the abundance relations of the individual atomic species, taken in connection with what has been presented before, make the evidence entirely conclusive. The tables and the figure of this section were prepared in order to prove that the Rutherford theory, that the light atoms are built up mostly of particles of mass 3, was not justified. From this standpoint the presentation here is unnecessary, since Rutherford has recently withdrawn his theory.

Table XXVI, which gives formulæ that express the atomic weight and nuclear charge of the most abundant isotope for all of the light elements of even atomic number, is of extreme interest.

FIG. 19.



Each corner where 4 lines meet represents a *possible* isotope. The interesting feature of the plot is that only certain corners represent *actual* isotopes, and these exhibit a more or less definite pattern. The heavy line from Ni^{60} to O has exactly the characteristics found in a similar plot of the thorium disintegration series. To the left of O the series extends two atomic numbers to carbon, and from Ni^{6} it extends two atomic numbers to the right to Zn^{64}_{4}. Of the 16 atomic species in this series all but one (K^{40}_{2}, which would be unstable) have been discovered. This plot gives *definite* evidence of the fundamental importance of alpha particles in the building of light atoms, since along the heavy horizontal lines the difference between two adjacent atomic species with respect to composition is that of one alpha particle.

This table expresses *the remarkable fact that for the six successive elements of even number, carbon, oxygen, neon, magnesium, silicon, and sulphur, the most abundant isotope has both a charge and a mass equal to a whole number times the charge and mass of the alpha particle.* With argon there is a slight irregularity in that the less abundant isotope meets this condition, while the adherence to the rule returns again in calcium. The elements of higher atomic number, titanium, chromium, and iron (and presumably nickel, 60, and zinc, 64),[41] show the same general relationship except that each nucleus contains two negative (cementing) electrons in addition, so there is also present in each case one alpha particle in excess of that required to give the nuclear charge; while the mass is still expressed by that of a whole number of alpha particles. This corresponds to the presence in these nuclei of a quadruple neutron, which may be called a helio group,

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[41] *Phil. Mag.*, 42, 332 (1921). Since this was first written nickel, 60, and zinc, 64, have been discovered.

TABLE XXVII.

Atomic Percentage of Atomic Species in Meteorites, Showing the Importance of the Weight 4.

Atomic weight	$4q$	$3q$	$4q$ not $3q$	$3q$ not $4q$	$4q+3$	$4q+2$	$4q+1$
Element.							
Carbon	0.12	0.12	...	...	...	...	...
Oxygen	53.16	...	53.16	...	...	...	...
Sodium	0.62	...	0.62	...	0.62	...	...
Magnesium	9.86	9.86	...	...	...	1.65	1.65
Aluminium	...	1.21	...	1.21	1.21	...	...
Silicon ^{28}	13.82	...	13.82	...	...	...	1.38
Phosphorus	...	...	...	...	0.06	...	...
Sulphur	1.46	...	1.46	...	...	...	...
Potassium	...	0.11	...	0.11	0.11	...	...
Calcium	0.97	...	0.97	...	...	...	...
Titanium	0.005	0.005	...	...	...	...	...
Chromium	0.13	...	0.13	...	...	...	...
Manganese	...	...	...	...	0.06	...	...
Iron ^{56}	12.30	...	12.30	...	...	...	...
Cobalt	...	...	...	...	0.04	...	...
			82.46	1.32	2.10	1.65	3.03

of the formula p_4e_4, where p represents a hydrogen nucleus or proton, and e a negative electron. The two cementing electrons correspond exactly in their function to the beta electrons which are shot off in pairs, but not simultaneously, in the radioactive disintegration series. Fig. 19, which is an enlarged section of Fig. 5, shows that Zn_4^{64}, Ni_4^{60}, Fe_4^{56}, Cr_4^{52}, Ti_4^{48}, Ca_4^{44}, A_4^{40}, K_2^{40}, Ca_0^{40}, A_0^{36}, S_0^{32}, Si_0^{28}, Mg_0^{24}, Ne_0^{20}, O_0^{16}, and C_0^{12} show exactly the form of a radioactive disintegration series. Of all of these atomic species, K_2^{40}, which is the one which should according to the theory be extremely unstable, is the only one which remains undiscovered.

It is remarkable that the few atomic species of this series shown in Fig. 19 make up 93 per cent. of the material of the *meteorites, and nearly as great a percentage of the surface of the earth, which fact, when combined with the fact that the relations are exactly those of the thorium disintegration series, seems to the writer to be conclusive evidence that the alpha particle is the principal group concerned in atom building,* in the region of the light atoms as well as in that of the radioactive atoms.

In addition Fig. 19 shows that Co, Mn, V, K_1^{39}, Cl_1^{35}, and P_1^{31}; Ni_2^{58}, Mg_2^{26}, and Ne_2^{22}; and also Sc_3, Sc_3^{45}, K_3^{41}, and Cl_3^{37}; K_3, and Cl_3 form three other similar series in that they have just the spacing due to alpha particles.

That the weight 4 is of extreme importance is shown clearly by Table XXVII, which gives the abundance of the atomic species in the meteorites. In the table q represents a whole number.

The totals of the columns in a similar table for the earth's crust are almost the same, except that the column $4q+3$ adds up about 8 atomic per cent., and therefore is much more prominent. In both tables the abundance of the atomic species whose atomic weights are divisible by 4 is much greater than that of those divisible by 3, and the latter seems to gain its relative importance only through the inclusion of those weights which are common to the column $4q$.

(*To be continued.*)

Diffusion of Certain Metals into Zinc.—At the recent (forty-second) meeting of the American Electrochemical Society, Walter G. Traub, of the senior class in Chemical Engineering, University of Wisconsin, presented a communication embodying some experiments that show that thin deposits of gold, silver, copper and brass electroplated on zinc will in time disappear, having been diffused into the zinc. Nickel does not appreciably diffuse, and, therefore, by previously coating zinc with nickel the diffusion of the other metals is prevented. These results are in extension of results that are recorded by Roberts-Austen. The subject of diffusion of two solid metals is discussed in some detail in his work on metallurgy. See, for instance, "Introduction to the Study of Metallurgy" (fifth edition, 1902, pp. 66–73). The old process of making steel is an example of the interpenetration of solids. That some of the common metals, especially those of low melting points, give off appreciable vapors at ordinary temperatures has long been known. These vapors will affect a photographic plate, the action being entirely different from that of radioactivity. Some experiments in this direction, by Leffmann, are recorded in this JOURNAL (1914, vol. 178, p. 743). H. L.

The Straggling of Alpha Particles by Matter. G. H. HENDERSON. (*Phil. Mag.*, July, 1922.)—When a beam of parallel alpha rays traverses matter, the several particles meet different experiences in passing through the atoms encountered. As a result of any cross-section of the beam there exist particles having quite different velocities, though Geiger has shown that at the start the alpha particles from radioactive material do not vary in velocity by as much as ½ per cent. Moreover, at the cross-section considered the ranges of the particles are different, that is, the distances the particles will proceed before they cease to be observable. "The alpha particles may be said to be straggled out, and hence the term straggling has been applied to this phenomenon by Darwin."

The Rutherford atom with its positively charged nucleus and its negatively charged satellite electrons lends itself to the calculation of the amount of straggling and accordingly theoretical computations have been made. On the other hand there are two experimental methods of measuring the same quantity. The first is somewhat indirect and depends on the ionization caused by the alpha rays at different sections of their path. The second is based upon direct counts of the number of particles at different parts of their path, and it is of necessity a laborious process since many particles must be counted.

The two results obtained from the experimental methods agree none too well, differing as they do by 50 per cent. or less, yet they do agree in furnishing values three or four times as great as those deduced by theory. "Furthermore the calculated straggling increases steadily with increase of range, while that observed is constant within the limit of error." This constancy the author interprets thus: "This can only mean that the excess straggling takes place only in the last two or three centimetres of the range. From experiments with gold foils which will be discussed later, it appears probable that the straggling is confined to the last few millimetres of the range." A group of gold leaves was located at different parts of the beam. It was found to cause more straggling near the end of the range than elsewhere. The significant feature in this investigation is that experiment brings to light certain features of straggling that the present theory is incompetent to explain. It is at the end of the range that the new effects are noted and it is just there that Shimizu, working on the paths of alpha particles made visible by cloud condensation, encountered still another departure from the behavior predicted by theory. "It is noteworthy that this anomalous behavior of the alpha particle occurs at low velocities, where practically no investigation of the scattering alpha particles has been carried out on account of the experimental difficulties of dealing with slow alpha particles." It may be well to keep in mind that the Rutherford atom was devised to account for a certain effect inexplicable by the views of atomic structure current at that time. If, after mature proving both of the experimental processes and of the theoretical deductions, they persist in remaining in contradiction, then our conception of the atom must be modified. G. F. S.

AN EXTRACTION APPARATUS WITH EXTRACT-RECOVERY AND SOLVENT-REGENERATIVE DEVICES.*

BY

LEWIS C. KARRICK,

Associate Oil-shale Technologist, U. S. Bureau of Mines,

AND

DOUGLAS GOULD,

Fellow, Metallurgical Research Department, University of Utah.

The more common laboratory extraction methods are not entirely suitable for the treatment of certain finely divided substances, largely because of the fact that the fine particles clog the filter medium during the downward flow of the solvent. The apparatus, described and illustrated, was designed particularly with a view to the elimination of filter clogging troubles, by providing a space above the layer of pulverized material as a means of settling the suspended particles before they reach the filter. It was also desired to prevent compacting of the material under treatment, and this has been accomplished by employing an upward flow of the solvent. The new device has been found to operate very successfully in the extraction of soluble matter from pulverized substances.

The drawing illustrates the essential parts of the apparatus, and the course which the solvent takes in passing through the system is indicated by arrows. The solvent enters the bottom of the extraction tube and passes up through the sample being extracted, then out of the tube by way of the settling space and filter. It then flows into the extract-recovery flask, in which it is vaporized. The vapors pass to the reflux condenser, and from there the condensed solvent returns to the extraction tube.

The extraction tube may be made of glass or iron, otherwise the entire apparatus is of glass. A two-inch iron pipe has been used as an extraction chamber and has been found to be satisfactory. In the bottom of the tube is placed a mat which may be made of a layer of glass wool covered with a piece of cloth. This is used merely to provide a support for the material to be treated and to aid in the uniform distribution of the solvent throughout the sample. A suitable filter is easily provided by using a Watman extraction thimble and fastening it around a one-hole cork-stopper through which is inserted a glass tube. The glass tube passes also through a cork-stopper in the upper cap of the extraction tube, thus providing a tight joint and allowing the filter to remain inside the extraction tube in contact with the solvent. Glass beads or a wire-gauze form should be placed inside the thimble to prevent collapsing of the filter. The solution, therefore, passes into the filter in a direction opposite to that usually employed, and then passes out through the glass-tube connection.

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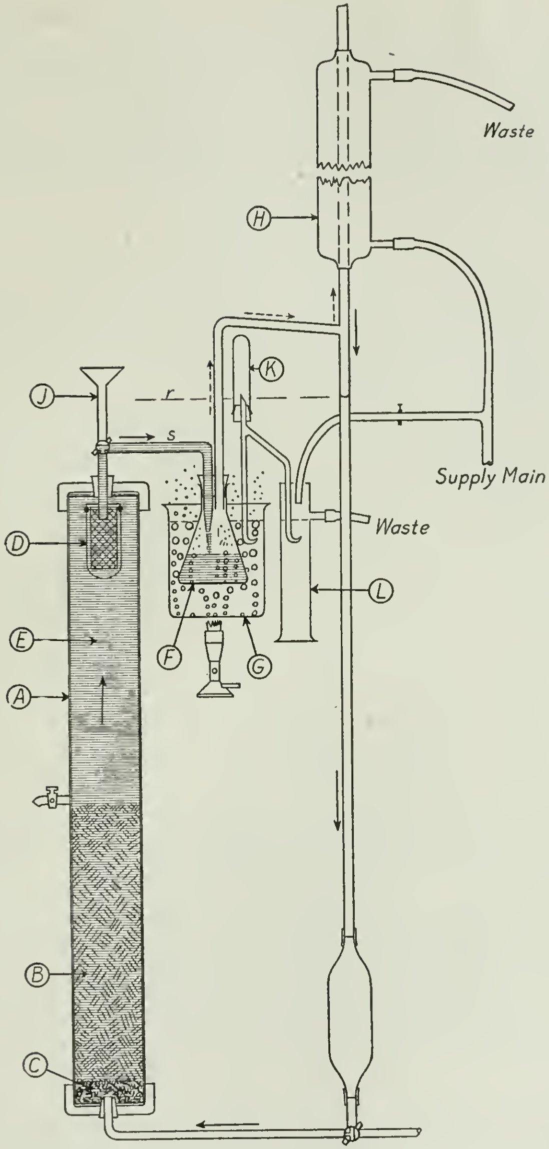
* Communicated by the Director of the Bureau of Mines.

If, as a result of too rapid circulation of the solvent, the filter should begin to clog, the filter-cake may be released by temporarily reversing the flow of the solvent through the filter. To do this fresh solvent is introduced through the funnel (*J*), while the cock below the funnel is turned so that the new solvent will flow into the filter and not into the side tube leading to the extract-recovery flask. The solvent in the return-pipe leading down from the condenser must first be drawn off by means of the drain-cock provided. Then with the drain-cock again turned to the position shown in the drawing the solvent will flow back out of the extraction tube and rise up in the pipe below the condenser, as the fresh solvent is simultaneously added through the filter and funnel. The filter will clog very seldom and, except in rare cases, it will not be necessary to clean it during an extraction test.

Obviously the entire system should be filled with solvent throughout the run and there should be sufficient solvent in the recovery flask at all times to keep the extract in perfect solution. Should it be desirable to remove the collected extract and replace the flask with a new one during the test, this can be accomplished readily without the loss of solvent. The drain-cock at the bottom of the condenser-tube must be turned so that the solvent contained in this tube, as well as the solvent in the flask, will be permitted to pass out of the system and collect in the new flask. When the extract in the first flask is practically free from solvent, the new flask containing the recovered solvent may be substituted in its place, and extraction resumed. This procedure will be found convenient as the end of the test approaches, since it will show by the amount of extract recovered in the flask how near to completion the extraction has progressed.

The rate of extraction may be varied at will. Since the



Extraction Apparatus with Recovery and Regenerative Devices.

A.	Leaching tube.
B.	Pulverized sample.
C.	Fibre mat.
D.	Filter.
E.	Settling space.
F.	Extract recovery flask.
G.	Boiler.
H.	Solvent-vapor condenser.
J.	Filter-washing and solvent-charging funnel.
K.	Siphon.
L.	Constant-level device.

velocity of circulation of the solvent through the system is dependent on the pressure-head "*r-s*," the head may be increased or decreased by varying the rate at which the solvent is vaporized from the flask. Therefore, the burner flame may be manipulated to bring about the desired rate of extraction. The bath (*G*) containing water, or other liquid of higher boiling point than that of the solvent, is placed around the flask so as to provide heating surface which is ample to cause boiling at the desired rate without danger of overheating the flask and damaging the extract in it.

In order that the apparatus may run continuously for several days at a time without attention, a constant-level device is provided which keeps the liquid (water in the case illustrated) at a definite height in the bath. *K* is a siphon and is an essential part of the constant-level device. The siphon is provided with a reservoir at its highest point to prevent an accumulation of air from interrupting its operation. This assures the continuous and uniform operation of the extraction apparatus.

When the extraction is finished the extract accumulated in the flask is freed of solvent by continuing the distillation until the excess solvent is removed and withdrawn from the system at the drain-cock below the condenser. Most of the solvent remaining in the extraction tube is drawn off at the cock placed in the side of the extraction tube. A certain amount of solvent will remain in the treated sample, and this may be entirely removed by distillation. By gently heating the sides of the tube with a flame (other means, if desirable), the vaporized solvent may be conducted out through the same cock and condensed by suitable means.

The device was designed and built for use in extracting from pulverized oil-shale the bituminous substance which is produced by heating the shale to its initial temperature of thermal decomposition. It has given perfect satisfaction and it is hoped that it will be found equally satisfactory for testing oil sands, leaching salt-laden earths, and for lixiviation purposes in general.

Germanium and the Marsh Test.—According to JOHN H. MÜLLER, of the University of Pennsylvania (*Catalyst*, 1922, vii, No. 7, 7), germanium hydride may be formed in the Marsh apparatus. Heat decomposes germanium hydride and causes the deposition of a reddish-brown metallic mirror, which might readily be mistaken for arsenic, since the common solvents for arsenic exert a similar action upon the mirror of germanium. J. S. H.

NOTES FROM THE U. S. BUREAU OF STANDARDS.*

EFFECT OF TEMPERATURE, DEFORMATION AND RATE OF LOADING ON THE TENSILE PROPERTIES OF LOW-CARBON STEEL BELOW THE THERMAL CRITICAL RANGE.[1]

By H. J. French.

[ABSTRACT.]

An apparatus for determining tensile properties of metals at high temperatures (including limit of proportionality) is described in detail. Included also are the results of tensile tests at temperatures from 20° to 465° C. of various grades of half-inch boiler plate including the following:

(1) A.S.T.M. firebox steel;
(2) Marine boiler steel;
(3) Railway firebox steel.

A section of the report is largely devoted to a discussion of the effects of different amounts of rolling at room temperature and at blue heat (300° C.) on the properties of such steels throughout the range given, and data are presented to show the effects of partial annealing, particularly at temperatures near the blue-heat range, on the cold and blue-rolled metal.

A series of experiments is described to show some effects of tensional elastic overstrain on the proportional limit, tensile strength, and ductility of low-carbon steel at different temperatures, together with the subsequent behavior of the steel in both tension and compression upon ageing.

A modified form of the original apparatus is described whereby several rapidly moving dials indicating both stress and strain are simultaneously and repeatedly photographed by a motion picture camera, when rapid rates of loading are used.

Included also are results of tests showing the effects of both rapid and slow loading on the tensile properties of boiler plate at various temperatures.

In the general summary is given a brief discussion of the observed effects in the light of the amorphous metal theory, and to illustrate typical fractures photomicrographs are included.

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* Communicated by the Director.

[1] Technologic Paper No. 219.

ELIMINATION OF WASTE—PAVING BRICKS.[2]

In accordance with the unanimous action of the joint conference of representatives of manufacturers, distributors, and users, the United States Department of Commerce, through the Bureau of Standards, recommends that recognized types and sizes of paving brick be reduced to the following list:

Standard Sizes and Varieties.

Standard Sizes.

Width	Depth	Length	Width	Depth	Length
Inches	Inches	Inches	Inches	Inches	Inches
3	4	8½	3½	3½	8½
3½	4	8½	3½	3	8½

Standard Varieties.

Plain Wire-cut Brick (vertical fibre lugless)			Repressed Lug Brick		
3	4	8½	3½	3½	8½
3½	4	8½	3½	4	8½
Vertical Fibre Lug Brick			Wire-cut Lug Brick (Dunn)		
4	3	8½	3½	3	8½
4	3½	8½	3½	3½	8½
. . .	. . .	. . .	3½	4	8½
Hillside Lug Brick (Dunn)			Hillside Lug Brick (repressed)		
3½	4	8½	3½	4	8½

Specific Example of the Application of the Principle of Simplification to the Paving-brick Industry.—This recommendation describes the need for eliminating economic waste caused by the excessive variety in types and sizes of paving bricks, and shows the procedure used in reducing existing varieties from 66 to 7.

The industry initiated the action through its trade association, and the Government, through the Department of Commerce, endorses and publishes as its own those simplifications recommended by joint conferences of producers, distributors and users of the commodity.

These Simplified Practice Recommendations when accepted by the entire industry serve as commercial standards of practice with consequent benefit through decreased stocks, costs, and investments, and increased sales, turnover and income.

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[2] Simplified Practice Recommendation No. 1.

NOTES FROM THE LABORATORY OF APPLIED SCIENCE, NELA RESEARCH LABORATORIES.*

IMPROVEMENTS IN PHOTOMETRIC EQUIPMENT FOR INTEGRATING SPHERES.

By **A. H. Taylor**, Physicist.

PHOTOMETRIC equipment in use with integrating spheres has not undergone any radical changes since the sphere was first introduced by Ulbricht. It usually consists of a bar photometer and accessories, including a set of standardized sectored disks and a Lummer-Brodhun photometer-head. In 1917, R. Von Voss,[1] in Germany, described a new type of photometer for use with spheres, but this does not appear to have come into use in this country. This laboratory has recently built apparatus designed along somewhat similar lines, but with several improvements which add to its convenience and usefulness.

The bar photometer used with the sphere usually has a candlepower scale attached to the comparison-lamp carriage, to read directly the candlepower of the lamp being photometered. In order to make this scale read correctly it is necessary to adjust the intensity of the comparison lamp by varying its voltage. This usually results in a color-difference between the lights compared. Another factor contributing to the color difference is selective absorption by the sphere paint. To overcome these color-differences it is necessary to prepare special color-filters, which is very difficult for most laboratories.

The apparatus built here is shown in the three illustrations. A suitable comparison lamp is enclosed in a rectangular box painted inside with the same paint as that used in the sphere. In the end of the box toward the photometer-head is an opal glass window, 8 cms. square, before which moves vertically a metal slide with a V-shaped opening. This slide carries a plate with three photometric scales, *viz.*, 25 to 75, 50 to 150, and 100 to 300 candles. Inside of the box at the top and bottom of the window are two horizontal broad bars (Fig. 3), the space between them being adjustable by handwheel *H*. Hence the vertical width of the luminous window is adjustable by means of the horizontal bars and the average horizontal width by means of the movable *V*. The area of the window is directly proportional to the distance from the apex of the *V* to the point midway between the horizontal bars. This window is placed about 30 cms. from the photometer screen and illuminates it directly.

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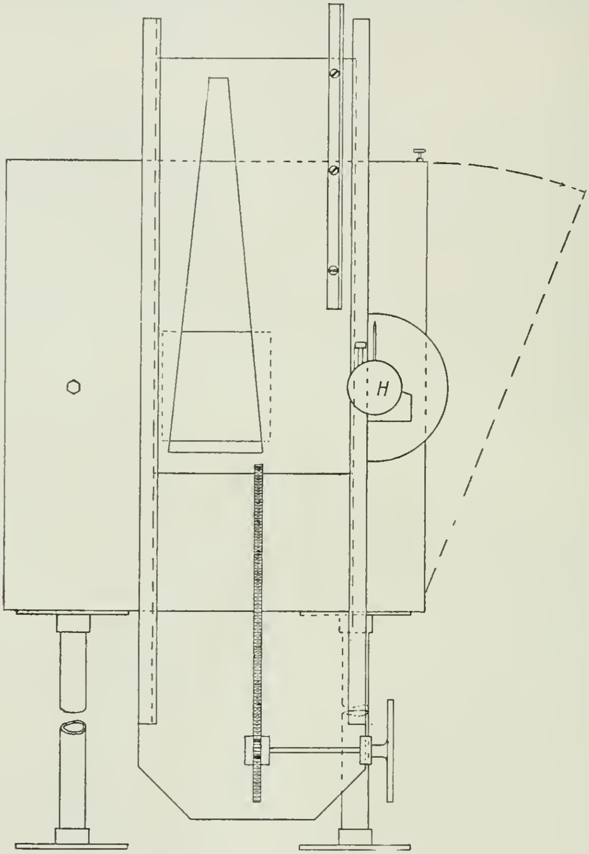
* Communicated by the Director.

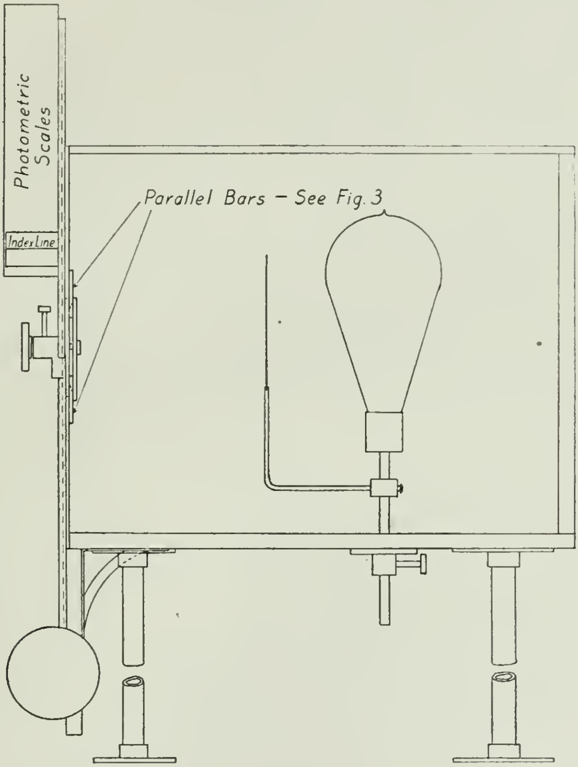
[1] E. T. Z., 38, p. 188, 605, 1917.

FIG. 1.



The sphere window, of a type originated by the Engineering Department several years ago, has two rough-ground flashed opal glass disks at opposite ends of a brass tube 4.5 cms. in diameter and white inside. The first disk is flush with the inner wall of the sphere, and the second disk is imaged in the photometer tube. Just behind the first disk is placed a removable, thin metal plate with circular opening. It is possible to pass from one photometric scale to another by inserting a metal disk with the proper size of opening.

FIG. 2.



Door removed.

In operation a perfect color-match may be obtained between the two lights compared without the use of any color-filters. The photometric scales are made to read correctly by means of the adjustable horizontal bars shown in Fig. 3.

As compared with any type of bar photometer this photometric equipment has the following advantages:

1. It is less expensive to build and install.
2. It requires much less floor space.

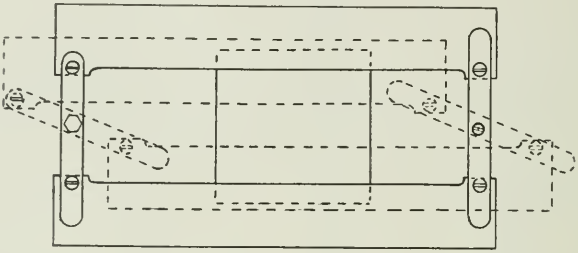
3. The photometric scales are uniformly divided, and for the highest precision a vernier may be used.

4. A perfect color-match may be obtained by the method described above.

5. The necessity for sectored disks is eliminated.

Tests made with this apparatus have proved it to be very satisfactory. A further improvement has been achieved by omitting the opal glass from the window in the box, and placing the lamp out of line of view from the photometer, so that the photometer screen receives its illumination from the wall of the box opposite the opening. This method has also been proven satisfactory by trial.

FIG. 3.



MAINTENANCE OF GLASS AREAS IN INDUSTRIAL PLANTS.

By M. Luckiesh, Director, and A. H. Taylor, Physicist.

It is apparent on every hand that the glass areas in industrial plants are not usually systematically and adequately cleaned. The various ribbed, rippled, pebbled, and clear glasses in use transmit from 70 to 90 per cent. of the incident light when clean. The accumulation of soot, dirt, rust, etc., results in a very great decrease in transmission factor in a comparatively short period of time.

The table shows the results obtained with seven glasses just as they were taken from industrial plants. It is seen that cleaning resulted in an increase in transmission factor of from four to fifteen times. This means that the daylight illumination intensity in these plants would be increased from four to fifteen times if the entire glass were cleaned. In other words, if the illumination intensity were only five foot-candles before cleaning it would be 75 foot-candles after cleaning glass No. 7. One of the glasses, No. 5, was so dirty that it was nearly opaque. Cleaning resulted in an increase in transmission factor of 250 times.

No.	Type of Glass.	Transmission.		Final Illumination Intensities in Terms of Initial Intensity.
		Before Cleaning.	After Cleaning.	
		Per cent.	Per cent.	
1	Plain clear	12	88	7.3 times
2	Plain clear	16	88	5.5 times
3	Fine ribbed	14	80	5.7 times
4	Fine ribbed	17	76	4.5 times
5	Fine ribbed	0.3	75	250.0 times
6	Wavy wire glass	13	80	6.1 times
7	Wavy wire glass	5	75	15.0 times

The investment in glass areas in industrial plants is considerable,[2] but the dividends from this investment are greatly reduced if the glass is not systematically and adequately cleaned.

A New Method of Measuring Corrosion Under Water. Investigation of Effect of Velocity. F. N. SPELLER and V. V. KENDALL.—Subaqueous corrosion is nearly proportionate to the concentration of oxygen dissolved in water, which fact is used for measuring the amount of corrosion in the experiments described. Water is passed through a certain length of ¼-inch, ½-inch, and ¾-inch commercial steel pipe uncoated, and the corrosion is measured by the difference in concentration of dissolved oxygen. Time of contact was held constant by varying the length of pipe. Velocities from 1/10 foot per second to 8 feet per second were obtained. Corrosion-velocity curves are given for each size pipe, for temperatures ranging from 60° to 170° F. Corrosion is found to increase with velocity in all cases, but at a decreasing rate. Rate of corrosion accelerates rapidly with rise in temperature over 90°, velocity and all other conditions being constant. This method of measuring corrosion is applicable to the investigation of the influence of other factors on subaqueous corrosion, such as composition of the metal, character of the water, etc. (A. C. S. Abstract Service.)

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[2] "Cost of Daylight," M. Luckiesh and L. L. Holladay, Abs. JOUR. FRANK. INST., **194**, 1922, p. 252; *Trans. Illum. Eng. Soc.*, 1922.

Resumption of Exchange Professorship.—The Karl Schurz Memorial Professorship in the University of Wisconsin was founded in 1910, for exchange professorships with the German universities. The exchange was interrupted by the war, but will be resumed in the coming academic year by lectures by Professor A. Sommerfeld, who holds the chair of Mathematical Physics in the University of Munich. Two courses will be given, one on Atomic Structure and the second either on the Analysis of Wave Propagation or on the General Theory of Relativity. The graduate school of the University also announces that Professor Svedberg of the University of Upsala will be present during the latter half of the academic year and will lecture and conduct seminars in the field of colloid chemistry. H. L.

The Removal of Small Amounts of Carbon Monoxide from Gas Streams by Passing Over Heated Granular Soda Lime. ROBERT E. WILSON.—The problem of the complete removal of CO from gas streams is of importance in a number of industrial applications. One or two German patents have mentioned the use of granular soda lime at fairly high temperatures for the purpose, but they offer no quantitative data. This paper describes a series of experiments at temperatures varying from 250° to 550° C. and using soda limes of varying composition. The results show that high alkali soda limes give complete removal at the lowest temperature (around 350° C.), providing water vapor was present and hydrogen absent. In the presence of considerable amounts of hydrogen, removal is not complete under any conditions tried. The fundamental reaction involved is apparently:

$$CO + H_2O + NaOH - Na_2CO_3 + H_2$$

(A. C. S. Abstract Service.)

Diffusion in Deformed Gels.—EMIL HATSCHEK (*Science Progress*, 1922, xvii, 86–94) has studied the diffusion of aqueous solutions of salts into deformed gels of gelatin. In one series of experiments, the gel contained lead acetate; when potassium chromate solution diffused into this gel, lead chromate (chrome yellow) was deposited in zones. In another series of experiments, the gel contained trisodium phosphate; when the solution of a calcium salt diffused into this gel, tricalcium phosphate was precipitated in zones. The shape and arrangement of these zones showed that it is highly improbable that the diffusion velocity varies with the varying degree of compression. Apparently the gel remains isotropic for diffusion under stress; and the velocity of diffusion is the same in a deformed gel as in an unstressed gel. J. S. H.

NOTES FROM THE RESEARCH LABORATORY EASTMAN KODAK COMPANY.*

SOME NEW SENSITIZERS FOR THE DEEP RED.[1]

By C. E. K. Mees and G. Gutekunst.

THREE dyes have been selected as having interesting properties from a number investigated. The first of these is naphthacyanole, prepared by the condensation of betanaphthaquinaldine ethiodide with quinoline ethiodide in the presence of formaldehyde in alcoholic potash, the dye being a homologue of pinacyanol. It sensitizes with a strong maximum in the deep red at $690\mu\mu$ and a minimum in the green.

Acetaminocyanole was prepared by the condensation of 6-acetaminoquinaldine ethiodide with quinoline ethiodide in the presence of sodium ethylate and formaldehyde. This gave a maximum at $730\mu\mu$. It was unstable in the presence of small amounts of water and is not thought to be generally useful.

Kryptocyanine was prepared by the condensation of lepidine ethiodide as described by Adams and Haller. In normal concentrations it gives severe fog, but in dilute concentrations good results are obtained, the maximum being at $760\mu\mu$. It is thus the most powerful sensitizer for the near infra-red known and is expected to have applications in astronomical photography. In the extreme infra-red, it is inferior to dicyanine.

Titrations.—J. L. LIZIUS and NORMAN EVERS (*Analyst,* 1922, xlvii, 331–341) have studied the titration of acids and alkalies. They recommend the use of "mixed indicators" for certain titrations. Thus phenol-violet, a mixture of 1 part of phenolphthalein and 6 parts of thymol blue, is used for the titration of weak acids; it gives a blue color at the neutral point and a violet color with alkalies. The results obtained by titration are increased in accuracy when the titrations are carried to a definite shade of color instead of to the change of color of the indicator. Observance of this procedure renders possible titrations which are otherwise impracticable.

J. S. H.

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* Communicated by the Director.

[1] Communication No. 147 from the Research Laboratory, Eastman Kodak Company and published in *Brit. Jour. Phot.,* 1922, p. 474.

Cod-liver Oil.—J. C. DRUMMOND and S. S. ZILVA have made a study of the Norwegian cod-liver oil industry under the auspices of University College and the Lister Institute, London (*Jour. Soc. Chem. Ind.*, 1922, xli, Transactions, 280–284). Extraction of the oil from the livers by the old rotting process is rarely practiced. However, the inactivation of the fat-soluble vitamine during the rotting is not as serious as might be expected. The oil is usually extracted by treatment of the livers with direct steam or in a steam-jacketed pan. From the viewpoint of preservation of the vitamine, the steam-jacketed pan is possibly slightly superior to direct steam. One of the chief aims of the more progressive manufacturers is to avoid oxidation of the oil. Posetran is a second fraction obtained in the extraction of the oil; it passes drop by drop through filter bags, yet does not suffer any appreciable loss of the vitamine. In the process of refining, the oil is cooled to a temperature of 0° to –10° C. in order to remove the stearine. At times, the oil may also be treated with an adsorbent, then passed through a filter press. This treatment removes pigments. The process of removing the stearine has an almost negligible result on the vitamine content of the oil. The stearine is the equal of butter, if not superior to that food, as a source of the fat-soluble vitamine. Therefore the stearine should be used as a food, although it is now applied for technical purposes. The modern white cod-liver oils are as valuable as the dark oils from the viewpoints of nutrition and medicinal value. J. S. H.

A New Form of Precision Hydrometer. C. W. FOULK.—This hydrometer consists of a glass float moving freely in a glass tube carrying a suitable scale. Between the float and the lower end of the tube a light chain hangs in a catenary curve. The float is ballasted so as to be in approximately submerged floating equilibrium in the liquid to be tested. The final adjustment to exact equilibrium is automatically made by the action of the chain, and this position of the float is then read on the scale. With a properly calibrated instrument density determinations accurate to one unit in the fourth decimal place can be made in a couple minutes. (A. C. S. Abstract Service.)

NOTES FROM THE U. S. BUREAU OF CHEMISTRY.*

ANALYSIS OF CRUDE VEGETABLE OILS.[1]

By George S. Jamieson and Walter F. Baughman.

[ABSTRACT.]

THE object of the existing methods for testing crude oils is to determine the quantity of refined oil that can be obtained from a crude oil when the refining is conducted in a particular way which simulates the commercial refining process. Some new methods have been developed by which it is possible to determine, among other things, the absolute quantity of neutral oil present. When a crude vegetable oil, dissolved in petroleum ether, is shaken with an aqueous potassium hydroxide solution, the free fatty acids are neutralized, the coloring matter is precipitated, and certain compounds of fatty acids other than glycerides are decomposed. Adding 50 per cent. alcohol causes the mixture to separate into two layers—a petroleum-ether solution of neutral oil and an alcohol-alkali layer containing the saponified fatty acids, coloring matter and other impurities. The two layers may be separated, the petroleum ether distilled from the ethereal solution and the neutral oil weighed.

It is possible to determine the quantity of fatty acids in the alcohol-alkali solution and also the quantity of alkali absorbed by the crude oil. Fatty acid glycerides are not decomposed by the method. A recovery of 100 per cent. of mineral oil was obtained by applying the method to dry neutral refined oil. Detailed directions for making this determination on cotton-seed, peanut, and soya bean oils have been prepared.

DEVELOPMENT OF PARATYPHOID-ENTERITIDIS GROUP IN VARIOUS FOODSTUFFS.[2]

By Stewart A. Koser.

[ABSTRACT.]

AN investigation was conducted to gain some idea of the ability of several type strains of the paratyphoid-enteritidis group to develop in miscellaneous foodstuffs, such as various vegetables, fruits, meats, and evaporated milk. The effects of different conditions, such as temperature of incubation, the hydrogen-ion concentration and the texture of the food, were considered in relation to multiplication and the ability to spread throughout the foodstuff.

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* Communicated by the Chief of the Bureau.

[1] Published in *Cotton Oil Press*, 6 (August, 1922): 33.

[2] Published in *J. Infect. Dis.*, 31 (1922): 79.

All the strains of the Gaertner group multiplied readily in the liquor of several common cooked vegetables, with the exception of the highly acid sauer kraut. In the fruit juices a rapid destruction of the organisms occurred. In several meat products Gaertner group organisms exhibited a marked ability to spread from one original point of inoculation throughout the foodstuff, although this occurred only under optimum temperature conditions.

The development of the Gaertner group in foodstuffs is usually not accompanied by visible alteration or spoilage. The present observations on this point are in accord with the reports of previous outbreaks of "food poisoning" caused by this group of organisms.

BY-PRODUCTS FROM CRUSHING PEANUTS.[3]

By J. B. Reed.

[ABSTRACT.]

CRUSHING whole peanuts by the expeller process usually gives a meal containing from 34.4 to 38.6 per cent. of protein. Crushing peanuts from which the hulls have first been removed by the hydraulic process gives a meal containing from 45.3 to 49 per cent. of protein.

Peanut meal is an excellent feed. Peanut hulls, however, have a low feeding value and can not be economically shipped any great distance for use as a feed.

It is possible to determine approximately the percentage of hulls in a mixture of peanut meal and hulls, either from the fibre content or from the protein content. It is probable, however, that the figures obtained from the fibre content will be more nearly accurate.

The composition of peanut skins removed by hand differs from that of peanut skins obtained from the peanut-butter plants. The composition of peanut germs is similar to that of the meats, with somewhat lower oil and somewhat higher ash contents.

A sample of meats from the Spanish variety of peanuts was found to contain 5 per cent. of sugars and 4.7 per cent. of starch.

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[3] Issued as U. S. Dept. Agr. Bul. 1906, August 12, 1922.

THE FRANKLIN INSTITUTE.

COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of Stated Meeting held Wednesday, September 6, 1922.)

Hall of the Institute,
Philadelphia, September 6, 1922.

Dr. James Barnes *in the Chair.*

The following report was presented for final action:

No. 2767: Audion. The Elliott Cresson Medal to Dr. Lee de Forest, of New York.

The following report was presented for first reading:

No. 2796: Noiseless Typewriter.

R. B. Owens,
Secretary.

MEMBERSHIP NOTES.

ELECTIONS TO MEMBERSHIP.

(Stated Meeting, Board of Managers, September 13, 1922.)

RESIDENT MEMBERS.

Mr. Roland L. Eaton, 20 South Eighteenth Street, Philadelphia, Pennsylvania.

Prof. Ernest Edward Johnson, Professor of Physics, Northeast High School, 2101 W. Ontario Street, Philadelphia, Pennsylvania.

NON-RESIDENT.

Mr. Robert Hatfield Irons, President, Central Iron and Steel Company, Harrisburg, Pennsylvania.

Mr. John E. Symons, Mechanical Engineer, The Texas Company, 17 Battery Place, New York City, New York.

CHANGES OF ADDRESS.

Miss Caroline D. Blackburn, 7028 Paschall Avenue, Philadelphia, Pennsylvania.

Mr. K. Braddock-Rogers, Trinity College, Hartford, Connecticut.

Mr. H. Calvert, President, Baird-Osterhout Company, 2114 Sansom Street, Philadelphia, Pennsylvania.

Mr. Edwin Frank, 1015 Shepard Avenue, Milwaukee, Wisconsin.

Prof. Arthur M. Greene, Jr., Princeton University, Princeton, New Jersey.

Dr. A. E. Kennelly, Harvard University, Cambridge, Massachusetts.

Mr. T. A. Lawes, 9794 Newton Avenue, Cleveland, Ohio.

Mr. Ralph H. Muller, 485 Rogers Avenue, Brooklyn, New York.

Prof. I. M. Rapp, The University of Montana, Missoula, Montana.

Mr. C. E. Sargent, P. O. Box 99, Clinton, Iowa.

Mr. S. Weinberg, Sunderland House, 35th Street and Powelton Avenue, Philadelphia, Pennsylvania.

MR. JAMES A. WRIGHT, Wright-Fisher Engineering Company, 600 McGill Building, Montreal, P. Q., Canada.

NECROLOGY.

EXCERPT FROM THE MINUTES OF A MEETING OF THE BOARD OF MANAGERS HELD SEPTEMBER 6, 1922, RELATIVE TO THE DEATH OF MR. COLEMAN SELLERS, JR.

Mr. Howson, in referring to the great loss which the Institute and the community have sustained in the death of Mr. Coleman Sellers, Jr., said that Mr. Sellers' service to the Institute and through the Institute to the Engineering profession could not be measured.

Becoming a Member of the Institute in 1873, he served for twenty-seven consecutive years on the Committee on Science and the Arts. In 1906, he became a member of the Board of Managers, in 1912 he was elected Vice-President, and in 1917 he was appointed Chairman of the Institute's Committee on Endowment.

On motion, duly seconded, the following preambles and resolutions were unanimously adopted:

Whereas, in the death of Mr. Coleman Sellers, Jr., Vice-President, the Institute has lost one of its best friends and strongest supporters,

Whereas, a deep sense of personal loss is felt by every member of the Board in the death of a friend, whose qualities both of heart and mind endeared him to all, therefore, be it

Resolved, That the Board of Managers of The Franklin Institute records with deep sorrow the death of its esteemed and distinguished Vice-President, Mr. Coleman Sellers, Jr., whose activities have been of inestimable value to the Institute and to the community.

Resolved Further, That a copy of the above preambles and resolution be forwarded to Mrs. Sellers.

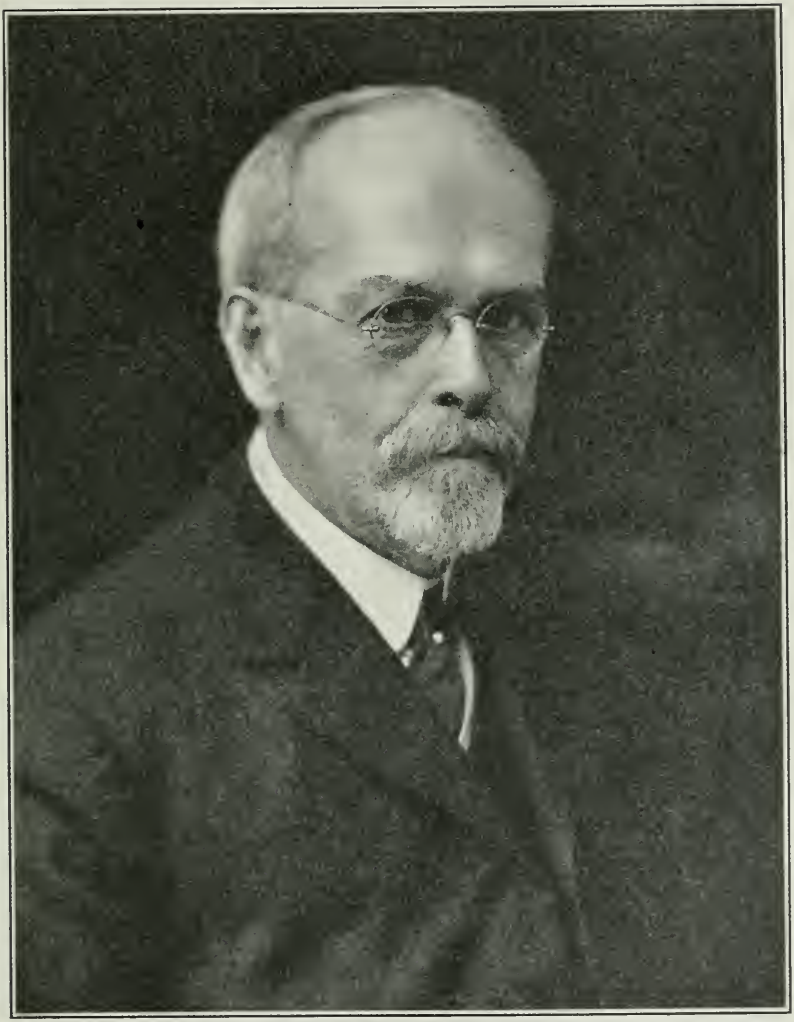
Resolved Further, That the above preambles and resolutions, together with the following biographical sketch of Mr. Sellers, be published in the JOURNAL.

Coleman Sellers, Junior, was born at Cincinnati, Ohio, September 5, 1852, the eldest son of Coleman Sellers and Cornelia, daughter of Horace Wells, a native of Connecticut, who with his father, Oliver Wells, established the Cincinnati Type Foundry.

In his paternal line he was of the sixth generation of progenitors engaged consecutively in the mechanical arts and who had contributed by useful inventions to their advancement. His father was the eldest son of Coleman Sellers, of Philadelphia, a mechanical engineer, whose firm built some of the early locomotives used in Pennsylvania and is credited with basic improvements in their design that have survived in their present construction. His wife was Sophronisba Peale, daughter of Charles Wilson Peale, the portrait painter of the Revolutionary period.

At the time of Coleman Sellers, Jr.'s, birth, his father was Superintendent of the Niles Locomotive Works of Cincinnati and a few years later in 1856 returned to Philadelphia as chief engineer and designer in the machine works of William Sellers and Company.

Coleman Sellers, Jr., was educated in private schools in Philadelphia and



COLEMAN SELLERS, JR.

entered the University of Pennsylvania in the Sophomore year, Class of 1873, and throughout his course was a First Honor man in his standing as a student. In University activities he held a prominent place, was Moderator of the Philomathian Society, Class President, Class Prophet, and finally Valedictorian at graduation when he received the degree of Bachelor of Science. In 1876 he received the degree of Master of Science after shop tests and thesis relating to steam boiler injectors.

Upon leaving college in 1873 he entered the works of William Sellers and Company under instruction to learn the trade and after experience as a journeyman machinist, he became foreman of a department, and in due time was transferred to the draughting room over which he was subsequently placed in charge.

Upon the incorporation of the firm he was appointed assistant manager and held that position from 1886 until 1902 when he was appointed Engineer; his father, Coleman Sellers, having previously retired from the business.

After the death of William Sellers, Coleman Sellers, Jr., succeeded him as President and Engineer and continued in that capacity until his death.

Although Coleman Sellers, Jr., is not credited with the inventions, such as marked the career of his father, his sound judgment, ingenuity and experience contributed in full measure to maintaining the high reputation of his Company as designer of machine tools and appliances in its special field.

While he did not seek public activities outside of his business, he accepted such duties as occasion offered both for the advancement of his profession and as a public-spirited citizen. He was one of the founders of the Engineers Club of Philadelphia and for fifty years active in The Franklin Institute lecturing on subjects in which he had special knowledge and serving on its various committees and for many years as one of its Board of Managers and as Vice-President.

From 1909 until 1913 he was President of the Chamber of Commerce of Philadelphia, and from 1908 until his death, one of the three State Commissioners of Navigation for the Delaware River and tributaries, taking particular interest in the training school for seamen conducted under its auspices.

In politics he was a Republican of independent principles and generally allied with reform movements without regard to party.

He was a member of the American Philosophical Society, the American Society of Mechanical Engineers, American Society of Naval Architects and Marine Engineers, American Academy of The Fine Arts, the University Club of Philadelphia, the City Club, Contemporary Club, Pennsylvania Society Sons of the Revolution and the New England Society of Pennsylvania.

During the late war, he was tireless in the discharge of his duties as head of the draft board in his district and in consequence of his devotion to the task his health was impaired, and to this circumstance is attributed the condition that led to his last illness.

In 1881 Coleman Sellers married Helen Graham Jackson, of Brookline, and is survived by one son, Coleman Sellers, 3rd, and three daughters.

His death occurred after an acute illness of several months, August 15, 1922, at Bryn Mawr, Pennsylvania.

Mr. John C. Bullitt, 3rd, 1811 Walnut Street, Philadelphia, Pennsylvania.

Prof. Jefferson E. Kershner, 445 W. Chestnut Street, Lancaster, Pennsylvania.

LIBRARY NOTES.

PURCHASES.

American Electrochemical Society.—Transactions, 1921.

American Institute of Electrical Engineers.—Transactions, 1921.

MÜLLER, C. F.—Zeitschriften und Zeitungsaddressbuch. Jahr. 14. 1922.

Poor's and Moody's Manual of Public Utilities. 1922.

Royal Society of London Philosophical Transactions, Series A, Volume 222. 1922.

SCARD, FREDERICK I.—Cane Surgar Factory. 1913.

Thomas' Register of American Manufacturers. Ed. 13. 1922.

GIFTS.

Acme Motor Truck Company, Acme Motor Trucks. Cadillac, Michigan, 1922. (From the Company.)

Allis-Chalmers Company, Small Steam Turbines, Bulletins 1123, 1124 and 1099B. Milwaukee, Wisconsin, 1922. (From the Company.)

American Aluminum Architecture Company, Booklet of Aluminum Roofing. Aurora, Illinois, no date. (From the Company.)

American Iron and Steel Institute, Annual Statistical Report for 1921. New York City, New York, 1922. (From the Institute.)

Automatic Refrigerating Company, Incorporated, Automatic Refrigeration and Refrigeration of Drinking Water. Hartford, Connecticut, 1922. (From the Company.)

Baker and Company, Incorporated, Data Concerning Platinum. Newark, New Jersey, 1921. (From the Company.)

Bayley Manufacturing Company, Bulletin 23 of Bayley Turbo Air Washers. Milwaukee, Wisconsin, 1922. (From the Company.)

Bristol Company, Bulletin 311, Recording Wet and Dry-bulb Thermometers. Waterbury, Connecticut, 1922. (From the Company.)

Brown Instrument Company, Catalogue No. 90 of Resistance Thermometry. Philadelphia, Pennsylvania, 1922. (From the Company.)

Buckeye Iron and Brass Works, Buckeye Brass and Iron Specialties. Dayton, Ohio, 1922. (From the Works.)

Canada Department of Mines, Summary Report, 1921, Parts A and D and Memoir 131, Kenogami, Round, and Larder Lake Areas, Timiskaming District, Ontario. Ottawa, Canada, 1922. (From the Department.)

Canadian Des Moines Steel Company, Steel Water Tanks for Public Service and Designs and Specifications of Standard Railway Water Tanks. Chatham, Ontario, Canada, 1922. (From the Company.)

Carnegie Steel Company, Wrought Steel Wheels. Pittsburgh, Pennsylvania, 1922. (From the Company.)

Chapman-Stein Furnace Company, Industrial Furnaces Bulletin No. 1. Mt. Vernon, Ohio, 1922. (From the Company.)

Charter Gas Engine Company, Catalogue No. 22, Charter Type "R" Oil Engine. Sterling, Illinois, 1922. (From the Company.)

Christiana Machine Company, Catalogue No. 101 of Gears. Christiana, Pennsylvania, 1920. (From the Company.)

Christiani and Nielsen, Booklet of Reinforced Concrete, Marine and Harbor Work. London, England, no date. (From the Company.)

Clark, James, Jr., Electric Company, Clark Electrically Driven Tools. Louisville, Kentucky, 1922. (From the Company.)

Cleveland Department of Public Utilities, Seventieth Annual Report of the Division of Water for the Year Ending December 31, 1920. Cleveland, Ohio, 1921. (From the Department.)

Columbia University, Bulletin of Information on Secretarial Studies. New York City, New York, 1922. (From the University.)

Dearborn Chemical Company, Pamphlet on Water. Chicago, Illinois, 1922. (From the Company.)

Dust Recovering and Conveying Company, Bulletin No. 508 of "Dracco" Pneumatic Conveying Installation. Cleveland, Ohio, 1922. (From the Company.)

Eastman Kodak Company, Abridged Scientific Publications from the Research Laboratory, Vol. iv, 1919-1920. Rochester, New York, 1922. (From the Company.)

Electric Furnace Construction Company, Electric Furnaces and "Electro" Steam Boiler. Philadelphia, Pennsylvania, 1922. (From the Company.)

Evens and Howard Fire Brick Company, Catalogue of Information for Use of Fire Clay Brick. St. Louis, Missouri, 1922. (From the Company.)

General Scientific Company, Catalogue R, Chemicals. Chicago, Illinois, 1922. (From the Company.)

Grand Rapids Public Library, Fifty-first Annual Report, April, 1921, to March, 1922. Grand Rapids, Michigan, 1922. (From the Library.)

Hercules Powder Company, Eliminating Waste in Blasting. Wilmington, Delaware, no date. (From the Company.)

Hoevel Manufacturing Corporation, Booklet of Hoevel Sandblast Machines. Jersey City, New Jersey, 1922. (From the Corporation.)

Hydraulic Society, Trade Standards in the Pump Industry. New York City, New York, 1922. (From the Secretary.)

Institution of Automobile Engineers, Proceedings Session, 1921-22. London, England, 1922. (From the Institution.)

Japan National Research Council, Proceedings No. 1, March, 1922, and Japanese Journal of Astronomy and Geophysics, Transactions and Abstracts, Vol. i, No. 1. Tokyo, Japan, 1922. (From the Council.)

Lamy, A., and Son, The Parson Ash Ejector. Elizabeth, New Jersey, no date. (From the Company.)

Lewis-Shepard Company, Catalogue of Lewis-Shepard Labor-saving Equipment. Boston, Massachusetts, no date. (From the Company.)

Lima Locomotive Works, Incorporated, Bulletins R-1, 2, 3-S, 4, and 5. Lima, Ohio, 1922. (From the Works.)

London Concrete Machinery Company, Limited, Catalogues 27 and 49. London, Canada, 1922. (From the Company.)

Lunt, W. S., Chinese Sugar Cane. Columbus, Ohio, 1857. (From the Philadelphia Book Company.)

MacGovern and Company, Incorporated, Catalogue 51. New York City, New York, 1922. (From the Company.)

Mills, Rhines, Bellman and Nordhoff, Several Ways to Reduce Foundry Costs. Toledo, Ohio, 1922. (From the Company.)

Maehler, Paul, Company, Maehler Ovens. Chicago, Illinois, no date. (From the Company.)

Maryland Institute for Promotion of Mechanic Arts, Year-book 1922-23. Baltimore, Maryland, 1922. (From the Institute.)

Massachusetts Charitable Mechanic Association, 127th Annual Report. Boston, Massachusetts, 1922. (From the Association.)

Meldrum-Gabrielson Corporation, Syracuse Adjustable Limit Snap Gage. Syracuse, New York, 1922. (From the Corporation.)

National Rifle Association of America, Official Program of the National Matches of 1922. Camp Perry, Ohio, 1922. (From the Association.)

New Mexico School of Mines, Catalogue 1921-1922 and Announcements for 1922-1923. Socorro, New Mexico, 1922. (From the School.)

New York Public Service Commission, Thirteenth Annual Report for the Year Ended December 31, 1919. Albany, New York, 1920. (From the Commission.)

Pacific Diesel Engine Company, Werkspoor Diesel Engines. Oakland, California, 1922. (From the Company.)

Parker, The Charles, Company, Catalogue No. 57 of Parker Vises. Meriden, Connecticut, 1922. (From the Company.)

Patterson-Kelley Company, Incorporated, Patterson Feed Water Heaters. Philadelphia, Pennsylvania, 1922. (From the Company.)

Pawtucket Manufacturing Company, Pamphlets of Tapers, Upsetting Machines, Open Die Bolt Threaders, Cold Punched Nut Presses, Key-seating Machines, Bolt Forging Machines and Shears. Pawtucket, Rhode Island, 1922. (From the Company.)

Philippine Islands Bureau of Civil Service, Twenty-second Annual Report for the Year Ended December 31, 1921. Manila, Philippine Islands, 1922. (From the Bureau.)

Prescott Company, Mine Pumps and Instructions for Installing and Operating Electric Pumps. Menominee, Michigan, 1922. (From the Company.)

Reeper Crane and Hoist Works, Catalogue 52. Reading, Pennsylvania, 1922. (From the Works.)

Rome Manufacturing Company, Rome Steel Tubing. Rome, New York, 1922. (From the Company.)

St. Louis Public Library, The Municipal Bridge of St. Louis. St. Louis, Missouri, 1922. (From the Library.)

St. Louis Water Commissioners, Annual Report for Year Ending April 1, 1922. St. Louis, Missouri, 1922. (From the Commissioners.)

Sampson Axcess System, Incorporated, Catalogue No. 2. Lynn, Massachusetts, 1922. (From the Company.)

Sargent, E. H., and Company, Scientific Laboratory Apparatus List No. 25. Chicago, Illinois, 1922. (From the Company.)

Scientific Materials Company, Optical Pyrometers. Pittsburgh, Pennsylvania, 1922. (From the Company.)

Sears, Henry D., Weber Dependable Wiring Devices. Boston, Massachusetts, 1921. (From Mr. Sears.)

Shoe and Leather Reporter, Annual, 1922. Boston, Massachusetts, 1922. (From the Shoe and Leather Reporter.)

Sizer Forge Company, Die Blocks. Buffalo, New York, 1922. (From the Company.)

Sturtevant, B. F., Company, Bulletin No. 294 of Stokers. Boston, Massachusetts, 1922. (From the Company.)

Tasmania Geological Survey, Progress of Geological Research in Tasmania since 1902, by Loftus Hills, and Underground Water Resources of the Jericho-Richmond-Bridgewater Area, by P. B. Nye. Hobart, Tasmania, 1922.

Taunton Water Commissioners, Forty-sixth Annual Report. Taunton, Massachusetts, 1921. (From the Commissioners.)

United States Air Service, Information Circulars Nos. 345, Report on Blower Used in Tests of Air-cooled Cylinders, and 356, Variation in Volumetric Efficiency of an Engine with Valve Lift. Washington, District of Columbia, 1922. (From the Chief of Air Service.)

United States Bureau of Census, Mortality Statistics for 1920. Fourteenth Census of the United States, taken in the Year 1920. Washington, District of Columbia, 1922. (From the Bureau.)

United States Department of Agriculture, Bulletin 1063. Washington, District of Columbia, 1922. (From the Department.)

United States Geological Survey, Bulletins 730-C, 735-E, 736-B and Pamphlets on Talc, Soapstone, Quicksilver, Bauxite, Aluminum, Asphalt, Gypsum, Tin, Mica, and Magnesite in 1921. Washington, District of Columbia, 1922. (From the Director.)

Uruguay Republica Oriental, Anuario Estadistico, Ano 1919. Montevideo, Uruguay, 1921. (From Oficina de Deposito, Reparto y Canje Internacional de Publicaciones.)

University of British Columbia, Calendar, Eighth Session, 1922-1923. Vancouver, British Columbia, 1922. (From the University.)

University of Colorado, Catalogue, 1921-1922. Boulder, Colorado, 1922. (From the University.)

University of Utah, Bulletin No. 16 of Summer Quarter Session. Salt Lake City, Utah, 1922. (From the University.)

University of Vermont, Catalogue 1921-1922. Burlington, Vermont, 1922. (From the University.)

University of Virginia, Adminstrative Report of the Virginia State Forester for the Calendar Years 1920-1921. Charlottesville, Virginia, 1922. (From the University.)

Victor Tool Company, Self-opening Die Heads, Collapsible Taps and Nut Facing Machines. Waynesboro, Pennsylvania, 1922. (From the Company.)

Wardman, C. B., and Company, Limited, One Hundred Years of Engineering. London, England, no date. (From the Company.)

Zeller Lacquer Manufacturing Company, Incorporated, 250 Lacquer Questions Answered. New York City, New York, 1922. (From the Company.)

BOOK NOTICES.

Molecular Diffraction of Light. By C. V. Raman, Palit Professor of Physics in the Calcutta University. 103 pages, 8vo. Printed by Atulchandra Bhattacharyya at the Calcutta University Press, 1922.

This book, a product of scientific activity at the Calcutta University and dedicated to the Vice-Chancellor, Sir Asutosh Mookerjee, attests the generous response of the Asiatic mind to the stimulus of western physical thought. The recent pages of the *Philosophical Magazine* have borne ample witness to the value and diversity of this reaction.

Such a volume as this cannot but be welcomed wherever throughout the world there is interest in understanding the phenomena of light. The author presents as the subject of the book the important question "Does any departure from perfect regularity of the light-propagation arise from the discontinuous structure of the medium?" and holds so well to the course he has laid out for his discussion that the reader who has followed the nine short chapters with comprehension feels himself to have advanced through familiar ground up to the very frontiers of the subject and, in addition, to know in just what direction to look for extensions of territory. Would that more physicists found time and inclination to write reports on the present status of limited fields of investigation with which they are familiar and in which they have made important contributions!

In gases the accepted theory of molecular diffraction is that proposed by the late Lord Rayleigh for the explanation of the blue of the sky. "The individual molecules in a gas through which the primary waves of light pass are regarded as secondary sources of radiation, each molecule acting more or less as it would in the absence of its neighbors." The mathematical development of this principle by its proponent leads to a relation between the wave-length of the incident light, the index of refraction of the medium and the intensity of the diffracted light that in the main explains in a satisfactory manner a large body of observed phenomena. The author examines the correctness of certain assumptions made in the derivation of this relation and concludes that their validity rests on (1) "the conditions being such that the compressibility of the medium is given with sufficient accuracy by Boyle's Law" and on (2) "the complete non-uniformity in the spatial distribution of the molecules in so far as very small volume elements are concerned."

In the second chapter are presented experimental results of the study of the scattering of light by gases. There is a marked difference between the polarization of the scattered light as predicted from the Rayleigh theory and as actually observed. Rayleigh accounts for this by assuming that the molecules possess three axes of symmetry and are oriented at random. Others have sought an explanation by using the Bohr-Sommerfeld model of the molecule but with little success.

When we come to the chapter on "Atmospheric Scattering and Twilight Phenomena," it is interesting to note how many references relate to American work. Abbot and Fowle, Luckiesh in the Journal of The Franklin Institute, Kimball and W. J. Humphreys are among these cited. With the last named, the author is in positive disagreement on one point. Humphreys holds that the conditions of the sky at dawn and sunset are so complicated that a rigid analysis leading to an adequate explanation of the light effects then occurring can scarcely be hoped for. Raman, on the other hand, states that twilight is due to the illumination of the dust-free upper portions of the atmosphere by sunlight which in its course has not traversed the dusty lower air, and claims that "We are entitled to regard the problem as one of practically simple molecular diffraction, and the complications arising from secondary scattering are far less important than might be imagined. Sufficient work has been done, however, to show that the problem of twilight, at least in its essential features, is capable of being subjected to numerical computation of intensities from theory for detailed comparison with the observations."

Lord Rayleigh as long ago as the end of last century emphasized the inapplicability of his theory of molecular scattering of light to the cases of liquids and solids. In the face of this some recent investigators have suggested that the theory mentioned may none the less be applied to liquids. The author combats the propriety of this, basing his objections on the failure of liquids to conform to Boyle's Law in their pressure-volume relations and further on their departure from the condition of complete non-uniformity of spatial distribution. The molecules of a liquid occupy in actuality a larger fraction of the volume of the containing vessel than do the molecules of a gas at ordinary pressure in the same vessel. In the former state, therefore, the molecules have less opportunity to depart from uniformity of distribution than in the latter. Since then the scattering of light by liquid molecules cannot be explained by Rayleigh's theory, recourse is had to the "theory of fluctuations" developed by Einstein and Smoluchowski, wherein the scattering of light is attributed not to the action of individual molecules, but to small local variations of density brought about by the heat agitation of the molecules. The formula for the intensity of scattered light derived from this theory is more general than that of Rayleigh. In fact, it reduces to the latter when certain relations characteristic of gases are introduced into it. An account is given of an attempt to compare values of intensity derived from the formula with observed values. In spite of the difficulty of getting a specimen of water free from motes, a satisfactory agreement was found. Yet this formula, which holds for such different conditions of matter as gas at ordinary pressure, gas near the critical point and a liquid, seems to cease to hold when the attempt is made to apply it to saturated vapors below the critical temperature. Careful experiments are greatly needed either to establish or to remove this discrepancy. Such experiments are now actually in progress.

The color of the sea is treated in a separate chapter and experiments of so interesting a character are described that it would seem a loss of opportunity for any physicist hereafter to take a voyage without a Nicol in his baggage. In the July, 1922, number of this JOURNAL, page 106, there is given some account of Raman's work on the color of sea water. He concludes that "The blue color of the scattered light is really due to diffraction, the selective absorption of the water only helping to make it a fuller hue."

The study of the scattering of light in crystals is in its incipiency. The effect has been observed in quartz, rock-salt and ice. Quantitative measurements are now being made in the Calcutta laboratory. Very little is known about the relations of amorphous solids to the scattering of light. Optical glass has a scattering power 300 times as great as that of pure air according to Rayleigh.

In the final chapter the relations of molecular diffraction to the quantum theory of light are discussed. "In the year 1905, Einstein put forward the hypothesis that the energy of a beam of light is not distributed continuously in space but that it consists of a finite number of localized indivisible energy-bundles or 'quanta,' capable of being absorbed or admitted only as wholes. The theory had some notable successes to its credit, especially the prediction of the photo-electric equation and the explanation of the phenomena of ionization of gases by X-rays. Nevertheless, it has been felt that very serious difficulties stand in the way of its acceptance." It is pointed out that this theory of Einstein lends itself well to an explanation of the experimentally found quantity of scattering in a highly compressed gas. Should it become established that the scattering mentioned is inconsistent quantitatively with the Einstein-Smoluchowski theory, then this, which is based on a continuous distribution of light energy through space, may need to be abandoned in favor of the quanta theory.

The book abounds in suggestions for fruitful experimentation. There is perspective in its treatment. One does not lose sight of the woods in looking at the trees. GEORGE F. STRADLING.

LIQUID FUEL AND ITS APPARATUS. By Wm. H. Booth, F.G.S., Member of the American Society of Civil Engineers. Second edition. 308 pages, illustrations, plates, 8vo. New York, E. P. Dutton and Company, no date. Price, $4.00 net.

The subject of liquid fuel has been a prominent feature of journal literature for several years. There is, indeed, a prospect of serious international complications over it, in view of the fact that oil supplies are not uniformly distributed, and the great maritime nations are now aware of the probability of oil-burning plants being generally established for motive power in ships. Extensive application has already been made, some of the largest passenger ships having been converted into oil-burners, with great saving as to labor and storage, but a new trouble has arisen, in consequence of the fouling of harbors and streams by the escape or discharge of oil.

The present work is an enlarged edition of one issued about a dozen years ago. In this interval great advances have been made not only as to the importance of liquid fuels, but in the apparatus for their use. The author attributes to Mr. Holden of the Great Eastern Railway of England, the first successful employment of liquid fuel in that country. He used surplus tar at first, but the road is now using Texas oil. The railways in southern Russia have used petroleum residuum for many years. In the preparation of this second edition, the author has searched the standard literature, and has also used information from manufacturers of apparatus, when such statements have seemed trustworthy.

The first really practical and efficient employment of liquid fuel for steam-raising purposes seems to have been due to Thomas Urquhart, who used it by means of a spraying system in locomotives on the Grazi and Tsaritzin Railway of Russia. An account of this appeared in the proceedings of the British Institution of Mechanical Engineers in 1884. The early liquid fuels were tars or residua; the modern liquid is mostly crude oil. Mr. Booth considers that the method has passed the experimental stage, yet the possibility of exhaustion of petroleum supplies always hangs like the Damoclean sword over the world. There seems to be no reason to fear early exhaustion of coal, but labor problems in coal mining are becoming more and more serious every day. The present production of mineral oil is a mere fraction of the coal production. Oil has a much higher calorific value than coal, being about 30 per cent. better, weight for weight, than the best coals. There is but one satisfactory way as yet known for burning liquid fuel, namely, by atomizing it.

This book gives a concise but clear and full account of the methods and apparatus employed in the use of liquid fuels and is a useful manual for motive power engineers. HENRY LEFFMANN.

THE CHEMISTRY AND TECHNOLOGY OF GELATIN AND GLUE. By Robert Herman Bogue, M.S., Ph.D., Mellon Institute Research Fellow and Research Chemist for Armour Institute. x-644 pages, 8vo. New York, The McGraw-Hill Book Company, 1922. Price $6.00 net.

Few substances employed in the industries are more familiar and have been longer in use than glue. In a purer form, termed "gelatin," it has found many applications wholly different from that for which it was originally employed. Notwithstanding the importance of these products, and the long time in which they have been known, the chemistry of them is still imperfectly known. The book in hand is a worthy effort to summarize the existing literature which is very extensive, but was not yet in book form. The existing text-books are not up-to-date. The subject is treated in this work mostly from the chemical point of view, and primarily for the student and research worker. Doctor Bogue gives us as an introduction, an interesting and and useful summary of the early history of the making and use of glue, which was prepared, as might be expected, first from the skins of animals. Here he unequivocally allies himself with those who regard man as an evolution from a lower order of animals. A granite carving, probably 4000 years old, found in Egypt, shows the working up of a tiger's skin and an allusion in the Iliad refers to the larding of an ox-hide for making it supple. Early allusions in Biblical and classic literatures are also noted. A frontispiece is a reproduction of an Egyptian carving of about 1300 B.C. showing the use of glue for veneering and joining. It is stated that the period is that of the Exodus, but there is an uncertainty about the date of that event. However, there is no reason to doubt that the carving is very ancient. The manufacture of glue in Europe was doubtless begun at an early period, but actual records seem not to go back of the last decade of the seventeenth century. The first mention in British patent literature is 1754. The substance was prepared from the tails and fins of whales and other fish refuse. Not long after a patent was taken out for the preparation of "isinglass," made from the internal membranous parts of fishes. The use of high-pressure boiling was introduced in 1822. An edible preparation was first the subject of a patent by Arney in 1846.

After these historical, etymological and statistical summaries, the chemistry and technology of the products are taken up. Over two hundred pages are devoted to the theoretical aspects. This section begins with a statement of the constitution of the proteins as a class, followed by a specific discussion of gelatin and its immediate allies. Large space is given to the physical chemistry of the gelatins, and then their characters as lyophilic and amphoteric colloids are discussed. Very extended and elaborate discussion is given to the latter questions and those who are not familiar with the existing development of colloid chemistry will find many curious and astonishing facts.

The technologic part covers a little more than half the book. The manufacture of glue and gelatin is treated by Ralph C. Shuey, M.S., of the Redmanol Chemical Products Company. This section covers all phases of manufacture, including hide glue, bone glue, ossein and gelatin, the last term, being by common consent applied to the finer varieties, especially those employed as food. In this line great care is necessary. The whole plant must be constructed so that entire cleanliness may be secured. As the vessels must be sterile, wooden containers are unsuitable, and as the liquors are generally kept slightly acid, some of the common metals are inapplicable. Aluminum seems to be the best. One of the dangers is that arsenic may be applied to the raw material as a preservative, and thus be found in the finished product. Some years ago the United States Government established minimum limits for arsenic in commercial gelatins. Sulphites are often used for bleaching and may also remain. This impurity is equally a matter of official control. Some years ago LaWall and Leffmann showed that some of the highest priced gelatins in the market (importations from Europe) contained considerable amounts of sulphites. The most objectionable impurity, at least the most frequent, is bacterial contamination. Unfortunately, as the author of the section points out, contaminated and even slightly decomposed stock is not infrequently put on the market and is not always easy to detect. He recommends a rigid system of factory inspection.

Other sections of the second part are devoted to water-proof glue, marine glue, testing of samples, detection of glue and gelatin, and the uses and applications of all grades. The detection of gelatins and glues, as well as of some carbohydrate products of similiar properties (*e. g.*, agar) has become an important part of the work of the food chemists, and those engaged in food analysis will welcome the excellent account which is given of the methods applicable to foods and other articles.

The book is a most welcome addition to our literature on the subject. A good deal has been written on the more abstruse phases of colloid action, but the work before us is a comprehensive and valuable summary of the special subject. The mechanical execution is excellent, the literary style commendable and the more than one hundred illustrations, including diagrams and apparatus, serve to make clear the statements. Good indexes and a number of useful tables add still further to the value of the work.

HENRY LEFFMANN.

THE CHEMISTRY OF COMBUSTION. By J. Newton Friend, D.Sc., Ph.D., F.I.C. 100 pages, contents, bibliography, notes and index, 16mo. New York, D. Van Nostrand Company, 1922. Price $1.25 net.

This book, one of a series of monographs of which several have already appeared, is the outcome of a lecture course at the Technical School at Birmingham, England. The chemistry of combustion has been a storm-centre in chemical theory for a long while. The disputes in the eighteenth century concerning phlogiston constituted a prominent feature in the science of that period. The deeper feelings of chemists were aroused over the attack and defense of the views. It is said that Cavendish relinquished his activities in research when he found that chemists generally were about to abandon the theory. Priestley was a stout defender of it. Doctor Friend's book is principally intended to set forth the present day views of the phenomena of combustion, hence discarded theories are given but little space. The subject of phlogiston receives but three pages, in which, however, a good summary is given of development of it. The term is due to Stahl. Reference is made to the Arabic writings of Geber in the eighth century, but it is doubtful whether the works thus ascribed are genuine. Bibliographical references enable the student to secure further details if desired. After this preliminary consideration, the author passes to the study of the chemistry of combustion under modern conditions and gives many data which are of great interest and value in the industries. At the present day when fuel problems are so complex and insistent, and when liquid and gaseous materials are steadily displacing the solids, all the physical and chemical questions concerning combustion are important. The nature of ordinary combustion was established in the latter part of the eighteenth century, although some faith in "phlogiston" lingered later, but many important points still remained incompletely observed until our own time.

The chapter on flame is an instance of the changing viewpoint. For many years, text-books have defined flame as "any volatile matter burning," but Doctor Friend defines it as a mass of gas raised to incandescence, and, therefore, recognizes flame without combustion, instancing a gas rendered luminous by electric discharge. The classic illustration of the candle flame is discussed at some length. Four zones are distinguished, and the long-received view that the luminosity is entirely due to incandescence of separated carbon is declared not wholly sufficient. Frankland, in 1867, showed experiments which threw doubt upon the common view (due to Davy) and ascribed the light to dense gases, but the question is not settled, and Doctor Friend thinks that the explanation of the phenomena of the candle may involve both views. We are not surprised that it is suggested that the luminous substance may be in the colloid condition. The book is well worth the attention of teachers and fuel engineers.

HENRY LEFFMANN.

STANDARD METHODS OF CHEMICAL ANALYSIS. Edited by Wilfred W. Scott, assisted by many collaborators. Third edition, thoroughly revised and greatly enlarged. Two volumes, 1567 pages, contents and index, 250 illustrations and 3 colored plates. New York, D. Van Nostrand Company, 1922. Price $10.00 net.

Thirty-six collaborators have taken part in the revision of this book, which has been so much increased in size as to necessitate presentation in two volumes. It covers a wide range of analytical work, and in consequence of the extensive share that specialists have had in its preparation gives to the chemist an up-to-date treatise. The preface enumerates many additions and extensions. The first volume is taken up with inorganic substances, giving special space to each important element; the second volume is devoted to important compounds and industrial products. Illustrations are freely used. The comparison plates of the spectrum by the prism and by the grating are very brilliant and well executed, but it is a question whether such illustrations are worth their cost. The worker who uses the instruments will obtain vivid pictures for himself, and will not be likely to rely on the plate, while to those who do not have the apparatus the plates can be of little value.

A work that has gone to the third edition within a little over five years, as shown by the date of the preface to the first edition, evidently has merit, and examination shows that it is comprehensive, clear and carefully written. The reviewer naturally turns to the chapter relating to the field in which he has especially worked, and in doing this is moved to wonder why, in describing the process for volatile acids in butter, the tedious alcohol saponification is given instead of the glycerol-soda method which is now generally used, being, indeed, the exclusive official method in several European countries. The mechanical execution of the book is good. The numerous illustrations have compelled the use of a very smooth shining paper that is not quite as agreeable to the eyes as the papers commonly used in scientific works.

In the space available for a review it is not possible to point out in detail the merits of the book or to advise as to material improvements if such advice is opportune. The fact that a large number of specialists have contributed articles, each one, of course, in the field to which he has given particular attention, ensures critical treatment. It might have been better to have made the book in several volumes to be sold separately, so that each purchaser could secure the part in which he or she is interested. Chemistry is now broken into so many specialties that a comprehensive work of this kind contains much that is of no interest to a particular worker.

Editing does not consist in merely choosing collaborators and reading proof; definite methods of spelling, syntax and form should be laid down. In the work in hand these rules have not been fully observed. References are in some articles quoted by year and volume, in others, by volume alone. The year should always be given. HENRY LEFFMANN.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS: Report No. 128, Aeronautic Instruments IV—Direction Instruments in Four Parts. By the Aeronautic Instruments Section, Bureau of Standards. 67 pages, illustrations, quarto. Washington, Government Printing Office, 1922.

This report, in four parts, covers the general field of direction instruments.

Part I points out the adequacy of a consideration of the steady state of gyroscopic motion as a basis for the discussion of displacements of a gyroscope mounted on an airplane, and develops the simple theory on this basis.

The principal types of gyroscopic inclinometers and stabilizers are briefly described and performance requirements stated.

Part II deals briefly with the testing and use of magnetic compasses for airplanes.

Part III contains a brief general treatment of the important features of construction of aircraft compasses, and descriptions of the principal types used in America and in foreign countries.

Part IV gives a brief history of the development of airplane turn indicators, with detailed descriptions of all known types and makes. The results of laboratory and flight tests are given for the several available gyroscopic turn indicators.

Report No. 146, The Six-component Wind Balance. By A. F. Zahm. 12 pages, illustrations, plates, quarto. Washington, Government Printing Office, 1922.

Report No. 146 is a description of the six-component wind-tunnel balance in use at the Aerodynamic Laboratory, Washington Navy Yard.

The description of the balance gives the mechanical details and the method of operation, and is accompanied by line drawings showing the construction of the balance. The balance is of particular interest, as it allows the model to be set up quickly and accurately in roll, pitch, and yaw, without stopping the wind. It is possible to measure automatically, directly, and independently the drag, side drag, and lift; also the rolling, pitching, and yawing moments. The balance can also be made self-recording.

PUBLICATIONS RECEIVED.

Space-Time-Matter, by Hermann Weyl. Translated from the German by Henry L. Brose. 330 pages, illustrations, 8vo. New York, E. P. Dutton and Company, no date. Price $7.50

Molecular Diffraction of Light, by C. V. Raman, Palit Professor of Physics in the Calcutta University. 103 pages, 8vo. Calcutta, University of Calcutta, 1922.

Select Methods of Chemical Analysis. A manual of analytical methods and general reference for the analytical chemist and for the advanced student. Edited by Wilfred W. Scott, Associate Professor of Chemistry, Colorado School of Mines. Third edition, thoroughly revised and greatly enlarged. Two vols., illustrations, colored plates, 8vo. New York, D. Van Nostrand Company, 1922. Price $10.

The Chemistry of Combustion, by J. Newton Friend. 107 pages, illustrations, 12mo. New York, D. Van Nostrand Company, 1922. Price $1.25.

Liquid Fuel and Its Apparatus, by Wm. H. Booth. Second edition. 308 pages, illustrations, plates, 8vo. New York, E. P. Dutton and Company, no date. Price $4.00.

U. S. Bureau of Mines: Bulletin 199, Experimental Production of Alloy Steels, by H. W. Gillett and E. L. Mack. 81 pages, plates, 8vo. Washington, Government, 1922.

National Advisory Committee for Aeronautics: Techanical Notes No. 108, The Use of Multiplied Pressures for Automatic Altitude Adjustments, by Stanwood W. Sparrow. 8 pages, illustrations, quarto. No. 109, The Twisted Wing with Elliptic Plan Form, by Max M. Munk. 7 pages, quarto. No. 111, Stresses Produced on an Airship Flying through Gusty Air, by Max M. Munk. 5 pages, quarto. Washington, Committee, 1922.

Crankless Engines (Aus.), Proprietary Limited, Handbook of the Crankless Engine. 37 pages, illustrations, plates, quarto. Melbourne, Australia, 1922.

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POSSIBLE CAUSES OF THE VOLCANIC ACTIVITY AT LASSEN PEAK.*

BY

ARTHUR L. DAY, Sc.D.,

Associate Editor, Member of the Institute.

My appearance before you to-day is due entirely to your watchful Secretary, who has discovered me searching for an earthquake within the boundaries of California and has very promptly summoned me to give an account of myself before this body. He has also asked me, very pertinently, to explain what I proposed to do with the earthquake in case I found it. It is a fair question.

Most of you will recall that on Memorial Day, in the year 1914, Lassen Peak broke out into activity with an explosion of ash-laden steam within the summit crater, which was witnessed by a number of people. Forest rangers climbed the mountain next day and found there, inside the old crater bowl, a small explosion-vent some 40 feet long and 25 feet wide with two cracks extending east and west from the opening to a distance of a hundred feet or more. The crater bowl was oval in shape, ten to twelve hundred feet in diameter, about 350 feet deep from the bottom to the highest point of the rim, and was rarely free

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* An address delivered before the Commonwealth Club of San Francisco on July 21, 1922.

(Note.—The Franklin Institute is not responsible for the statements and opinions advanced by contributors to the Journal.)

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from snow at any season of the year. In the winter time the accumulation of snow usually amounts to 30 or 40 feet, which does not melt to any considerable extent at this elevation (10,466 feet) before the middle of May. The explosion was followed by considerable steaming, and the rangers noted streams of water from the melting snow pouring into the small explosion vent and the cracks extending out from it. Very little attention has been paid to these two cracks by anyone who saw them or who has since learned of their existence. I shall ask you, however, to bear these in mind, for they have much to do with the search for the earthquake for which I am to account to you.

Other explosions followed this one at intervals of two or three days throughout the summer and autumn, increasing gradually both in duration and intensity. Many of the more powerful outbreaks lasted for four or five hours and steam clouds, black with ash, rose to a height of 10,000 feet or more above the summit. The country roundabout the mountain was strewn with ash and stones up to a foot or more in size for two or three miles. These rested on the snow during the early eruptions, and as long as the snow lasted, showing that they were quite cold at the time when they were thrown out. In the winter season following, no very accurate record was kept of these occurrences, for the mountain is shrouded in cloud and snow during that season and is often invisible for periods of several days or weeks.

The explosion vent grew in magnitude during this interval until it included nearly all of the old crater bowl. An ascent over the snow in March of 1915 showed a hole nearly a thousand feet in diameter, with steam emerging at several points, notably at the west end, where there was a notch in the rim toward which one of the two original cracks had been directed.

This gradually increasing activity culminated on the night of the 19th of May, 1915, almost exactly a year after the first eruption, in a terrific outbreak, followed by a mud flow on the northeast slope of the mountain, which devastated the valleys of Hat Creek and Lost Creek for some twenty miles.

It was on this evening also, about nine o'clock, when the only authentic appearance of red-hot rocks was noted. Mr. J. R. Milford and a party of friends were watching the volcano from the windward (west) side, which was the only direction from which it was clearly visible on that night. Mr. Milford has given a very graphic description of the glow at the top of the mountain illuminating the great cloud, and the gradual appearance of a red line marking the notch in the crater rim on the west side, which grew in intensity until the crater seemed to overflow like a great pot of slag forming momentary trails of red down the western slope of the peak. This operation he saw several times repeated between the hours of nine and ten, after which the activity diminished until it was no longer visible.

Closer inspection of this side of the mountain afterward does not verify all the details of Mr. Milford's description, though there is no doubt that he saw glowing material at the summit and the glow on the clouds. There is no appearance of flow structure in the lava which now fills the western notch, and furthermore at the temperature of red heat this lava is solid, not liquid. It was therefore not a lava stream which he saw, but the volcano plug itself thrust upward into the notch as a result of the pressure from below, during which red-hot material, though still solid, was exposed. The breaking up of these hot rocks and the fragments which rolled down the mountainside gave to Mr. Milford the impression of flow movement at a distance of twenty miles.

Notwithstanding the spectacular character of this appearance of red-hot lava and the tremendous explosions with which it was accompanied, this was not the most conspicuous effect of the night's activity. On the northeast slope of the mountain a mud flow developed which passed down Lost Creek and over the divide into Hat Creek, then following and laying waste both valleys for twenty miles or more to the northward. Newspapers and contemporary publications represented this mud flow to have come directly out of the crater, but this was not the case. Mr. B. F. Loomis, of Viola, one of the keenest observers of the mountain during this period, states this case briefly and succinctly:

" I do not believe that any hot water poured out of the crater as such at any time. Of course not. It is unthinkable that water, either cold or hot, would flow over the crater rim in gentle ripples while hot rocks and mud bombs were being hurled into the air a mile."

More deliberate observation afterward reveals the fact that the first evidences of the mud flow occur about 1500 feet below the summit. Here, in a bay of the mountain, there was stored up from the previous winter, a mass of snow and ice which is never completely melted in a normal year. Its depth has been variously estimated at from 50 to 100 feet. With such a mass of snow upon which the condensed steam and hot ash from the fearful explosions of that night fell, abundant material was furnished for an avalanche down Lost Creek Valley from 10 to 20 feet in depth.

Still, such an avalanche of mud and water, fearful though it was, would not have created the devastation afterward found there, without the release of forces of even more awe-inspiring magnitude. The Forest Service estimates that five million feet of primæval forest timber stood in this valley before the eruption of May 19th. Afterward it was completely gone, not a stump or root or trace of snow remained to indicate what had been on the valley floor before this eruption. Indeed the trees were removed for some hundreds of feet above the uppermost limit reached by the flood.

There is only one agency competent to account for such complete devastation, and that is a horizontal blast from the crater itself, shot directly into this mass of timber and snow. Furthermore, there is abundance of direct evidence of the progress of this blast, for on the sides of the valley far above the boundaries of the mud flow, trees are down which were not removed, and they lie without exception with their tops pointing straight away from the crater in spite of the fact that they lie upon steep hillsides. Not only this, but every tree has been subjected to a terrific sandblast, which has carried away the bark on the side toward the volcano while it remains undisturbed on the protected side. Trees which are broken off instead of uprooted have left behind stumps completely rounded off by the blast, and grains of volcanic sand have been driven into these trunks for an inch. These corridors of parallel tree trunks extend for nearly two miles on both sides of the valley far above any point reached by the flow of mud.

It could also be observed in the weeks following this eruption that the foliage of the standing trees on the borders of the devastated area was singed by the heat of the blast. Farther on in the region beyond the mouth of the valley, where the blast had spent its force, all the foliage was brown for a half mile or more.

Notwithstanding this no fires were kindled, which would seem to indicate plainly either that the blast was momentary or that its temperature fell somewhat short of the temperature necessary to kindle even dead twigs. Probably both of these conclusions are justified.

The total extent of the blast was about four and one-half miles in a direct line from the mountain summit, and the width of the zone of complete devastation was about a mile and a quarter at its widest point. Notwithstanding this catastrophic outburst there was no eye-witness of the occurrence of any of these phenomena. It happened at night and the first evidence of it to reach the public came in a telegram from the forest ranger stationed on Hat Creek, several miles below, who reported a devastating flood of milk-warm water and mud which was covering the meadows in the northern reaches of Hat Creek Valley, carrying away outbuildings and rendering the cattle ranches uninhabitable. Fortunately the number of persons in the valley thus early in the season was small and no live stock had yet been brought in, so that no actual loss of life occurred, but it is safe to say that if a city had been located in Hat Creek Valley at the point where it came under the direct power of the blast, as was the case in the great eruption of Mt. Pelée in Martinique (1902), the loss of life might have been as complete as it was then.

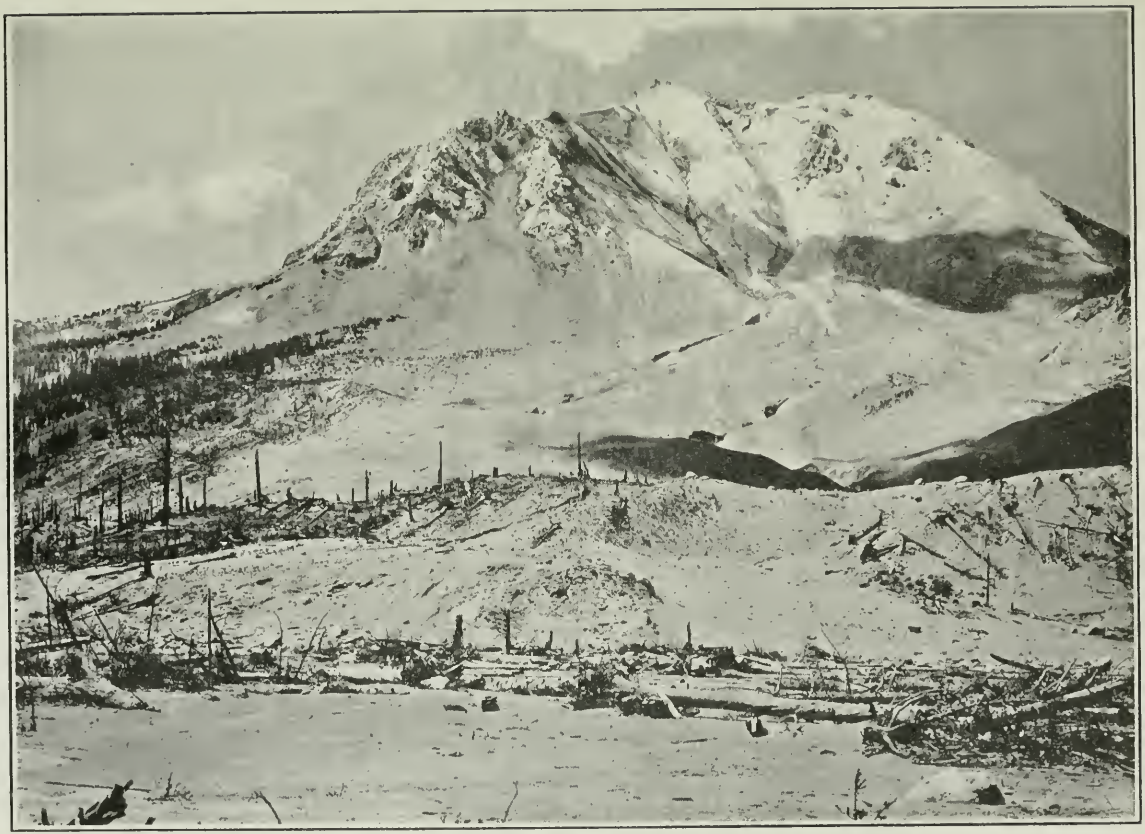
Following this outburst the volcano remained active more or less continuously during the next three days, being shrouded in smoke and difficult of observation during most of that period. At five o'clock on the afternoon of the 22nd came the greatest eruption of all, in which the volcano cloud rose to a height of more than five miles and could be plainly seen for a hundred miles or more in any direction. This was the culminating outbreak of the entire period of activity. Since that time the explosions have diminished gradually in violence until 1918, when they ceased entirely.

This culminating eruption of May 22, 1915, was also accompanied by a horizontal blast bursting from the same opening and proceeding in nearly the same direction as the previous one. The snow and the trees having been carried away for the most part by the first blast, less water and mud were available for the second flow, and practically no fresh damage was done. On the north slope of Lost Creek Valley a number of trees which had escaped the first blast were laid down like the earlier ones in parallel rows directly away from the crater, regardless of the lay of the land. In both of these blasts boulders up to 15 or 20 tons in weight were dislodged from the top of the mountain and borne by the flood into the valley below, some for a distance of five or six miles.

The mechanism of these horizontal blasts is interesting. At the beginning, or shortly before the activity of the 19th, the crater floor was raised from below until it stood nearly level with the crater rim, a vertical movement of more than 300 feet. Had it gone higher the plug would undoubtedly have been dislodged from the vent entirely, and a flow of lava would have resulted. As it was the enchained pressure of volatile matter (mainly water) within the mountain appears to have found vent on the 22nd without actually blowing off the top of the mountain, and thereafter to have remained powerless to open the main crater conduit. It was as though the lava plug with which the volcano had remained sealed for so many years had been started upward by pressure from within which had then found release at the weakest point in the inclosing chamber. This happened not to be through the plug itself but below the plug on the northeast side of the mountain, much as a gas explosion in a kitchen stove might do, raising the lid and escaping in a horizontal blast from beneath it. After the emergence of these horizontal blasts the pressure was released and the lid collapsed. Its present appearance indicates rupture by such forces at a great many points of the exposed surface.

The mechanism of this entire sequence of volcanic activity can, I think, be inferred quite simply from the phenomena which have been described to you, and an appropriate application of the laws of physical chemistry. The great volcanic clouds, which characterized the explosions, were mainly of dust-laden steam. There is extremely little evidence of the participation of sulphur or other chemically active ingredients from beginning to end of this series of outbreaks. This will serve to establish the fact that no heat arising from chemical action within the volcano contributed to the reactions which occurred. This conclusion is supported by the further observation that, with a single minor exception, no fires were kindled by the blast, and, with the exception of the night of the 19th of May, 1915, no evidence of red heat was visible on the top of the mountain. Compared with other volcanoes which have been studied the volcanic phenomena at Lassen Peak occurred at comparatively low temperatures, certainly not above red heat. Also it should be noticed that Lassen Peak is located in a region of considerable rainfall, that the summit crater is almost never

FIG. 1.



View of Lassen Peak from the northeast showing the devastated mountainside together with the upper valley of Hat Creek and Lost Creek taken from a point between four and five miles from the summit, July 22, 1915.

free from snow, and that several streams of considerable size have their sources high on the flanks of the mountain. We are therefore dealing with a cooling volcano hearth in a region of abundant water supply.

Considering such dynamic systems, it is usual to assume that temperature and pressure rise and fall together. If the temperature were to rise the pressure would be increased, and if it were to fall the pressure would fall with it. In such reasoning, however, we overlook a vital factor in the consideration of silicate systems in the presence of considerable quantities of water. Laboratory measurements have shown that silicate solutions (rock magma) of high silica content easily take up ten or fifteen per cent. of water when in liquid condition under pressure and carry it in solution. In accord with this we also find in nature occasional pitch-stones and obsidians, which have cooled from the magma without crystallization, also containing 10 per cent. or more of water. On the other hand, crystalline rocks, as shown by the thousands of analyses made of them, contain no more than 1.5 per cent. of water. In order to crystallize, therefore, a high-silica magma, containing 10 per cent. of water, must divest itself of more than 80 per cent. of this water in the process of crystallization. Such a large proportion of the water content set free in the hot volcano chamber will increase the pressure enormously, even though the crystallizing operation is a cooling process.

By way of illustration of this, silicate mixtures have been prepared in the laboratory, inclosed in bombs with a sufficient quantity of water, and the pressure measured over a series of falling temperatures. It has been demonstrated, for example, that a simple mixture of silica, potash and water, which begins to crystallize at 500° C., will discharge this water when the temperature is lowered from 500° to 420° and the water thus set free will immediately develop a pressure appropriate to that high temperature. In this system the pressure may increase seven-fold (from 50 atmospheres to 340 atmospheres) in cooling through this interval of 80 degrees.

Without going further into the physico-chemical details, this process finds direct application at Lassen Peak. The magma is an andesite, high in silica, and so far as we have evidence of the heat conditions it is in process of crystallization at a comparatively low temperature. The available water in the region is abundant to support the assumption that the percentage of water carried in the magma is large. The enormous quantities of water given off in the 300 or more explosions of record, some of which continued for several hours, still further support this assumption. The increase of water pressure depending upon the progress of crystallization is therefore appropriate to explain such a long series of explosions.

If this exposition has been clear Lassen Peak has been shown to be a true volcano and not a geyser, as sometimes asserted, that is to say, a chamber in which liquid magma (lava) is gradually crystallizing, located in a region which supplies to it an abundance of water. All of the explosions were steam explosions to which was added only the dust carried in the conduit or generated by attrition during the explosions. It is therefore from the engineering standpoint a cooling system to which no new energy is being supplied through chemical action of the kind which is characteristic of the volcanoes of Hawaii or of the Mediterranean.

It has been shown by laboratory experiments, in which all the factors were strictly measurable, that a silicate solution (lava), when crystallizing, sets free all of its water content above one or two per cent., and this water discharged in a closed chamber at a temperature of 600 or 700 degrees generates an enormous pressure within the chamber which may be sufficient to burst its bounds at the point of greatest weakness.

It remains to consider how such a process can produce a succession of explosions of gradually increasing intensity up to a culminating point and then gradually subside.

It is at this point that I wish to recall to your attention the two cracks in the crater floor which were discovered by the Forest Rangers shortly after the very first explosion at the summit. Considered as an explosion, this first outbreak was insignificant and not by any means adequate to explain the cracks. Still less are we able to recognize in it the outburst of 200 years of gradual crystallization and consequent accumulating steam pressure following the process above outlined. Such cumulative stresses should have been sufficient to blow off the top of the mountain, as once happened at Bandai San in Japan and at Katmai in Alaska. Suppose, however, that the temperatures within the mountain were relatively low, as every indication during the period of explosive activity seems to establish, then crystallization was probably proceeding at a very slow rate in a magma of high viscosity which very probably was much undercooled. By that I mean that the liquid magma was so inert that crystallization was lagging, although it had already reached a temperature considerably below that at which crystallization would have occurred under more favorable conditions. Suppose further that into this inert mass there was suddenly introduced, through cracks at the top, a body of water, under a pressure head appropriate to the height of the mountain, which was speedily transformed to steam, which, under such circumstances, we know is quickly absorbed by the magma. The first effect of such an intrusion is to cause a considerable increase in the fluidity of the lava, and this in turn a considerable increase in the rate of crystallization. Water is coming in at a low pressure from one source, and in consequence of it water is released from another source (out of solution) at a high pressure. An increased rate of crystallization means an increased rate of setting free of the water content already impounded in solution in the inert lava. The resulting pressure increase might be expected to seek an outlet through the opening which had thus been broached in the crater floor, and a small explosion might result. An undercooled lava system, though inert if cool enough, is unstable, and once it is set in action through local increase of fluidity in this manner, the tendency to reach equilibrium (through crystallization) is strong. Consequently the action here indicated is likely to proceed rapidly and the rapidly accumulating pressure to find relief in successive explosions depending for their magnitude and frequency directly upon the rate of advancing crystallization and the increasing amount of participating magma as the successive explosions expose greater masses to the new and favorable conditions. This seems to me to account well for the low intensity of the initial outbreak and the gradual increase in volume and intensity as the crater floor was shattered by successive explosions and greater quantities of water were admitted to the volcano hearth, bringing an increasing quantity of crystallizing magma into an action which eventually becomes more or less self-perpetuating until all the available uncrystallized magma is participating. Then follows the culmination and subsidence.

This analysis, if correct, might lead to two alternative results. That the potential activity (pressure) within the mountain is due to advancing crystallization, appears to be logically grounded and established by appropriate laboratory experiments. It could find release only in the breaking down of the resistance of the containing envelope, that is, the mountain itself. This might happen either from without or from within. If the release had come solely through accumulated pressure within, which eventually became adequate to overcome the normal resistance of the mountain, then a terrific explosion must have resulted through which the entire accumulation of energy would have found release in a single catastrophe. This obviously was not the case. If, on the other hand, the resistance of the mountain to the accumulated pressure within had somehow been weakened slightly by action from without, such as an earthquake crack, and this development of structural weakness had been followed by a succession of explosions extending it gradually, then we would seem to reach the counterpart of the present phenomenon.

It is for this reason that your Secretary found me searching for a record of an earthquake in California, one that occurred in April or May of 1914. Lassen Peak region is subject to earthquake disturbances, often of very noticeable magnitude, but no record exists of these local disturbances, either of their intensity, their direction, or their probable origin. So far as any records now available are concerned, we may not know whether the local earthquakes are to be regarded as possible causes or as effects of volcanic activity. For this reason I have been unable, so far, to verify my hypothesis fully, though I entertain no doubt of its substantial correctness, even without the record.

Speaking before the Commonwealth Club I feel free to emphasize our lack of knowledge of California earthquakes, for it was in this body, less than a year ago, that resolutions were passed urging a systematic study of the earthquakes of the west coast. It is probable that the need for such information in connection with volcanic activity at Lassen Peak will not impress you as a conspicuous and tangible need when compared with the need which is felt by engineers in the consideration of such problems as the proposed viaduct across San Francisco Bay, or the construction of buildings in regions peculiarly exposed to earthquake disturbance, or in connection with the water supply of our great cities, which, on this coast, frequently has to be drawn from the mountains many miles away. These are vital problems in California, and it is a pleasure to see that this representative body stands ready to defend them as such. Anything less than systematic study and record is of little value in considering earthquake phenomena, as I will illustrate to you in a moment.

As a beginning of such study it will be interesting to you to know that on July 1st the U. S. Coast and Geodetic Survey began a new primary triangulation to extend from points on San Francisco Bay to Reno, Nevada, with the definite purpose of ascertaining whether or not there is a northward creep of the coastal region such as has been reported probable by the astronomers at Ukiah and at Lick Observatory. It is of the utmost importance to establish definitely whether there is such a creep or is not. For if the creep exists, and by its northward movement sets up a strain in the earth's crust, and if this crust when strained to the limit ruptures, producing earthquakes like that of 1906, then it is of the utmost importance that we should know the direction and rate of this drift, that we should know where the lines of weakness are located, where previous ruptures have occurred, which of these continue to be active and which are no longer so. This a primary triangulation will reveal.

It will interest you further to know that the U. S. Geological Survey, in coöperation with the Universities at Stanford and Berkeley, the Branner Society in the south, and the Seismological Society of America, whose President, Professor Willis, is with us to-day, have already been at work throughout the year gathering together information about these breaks or faults with the purpose of publishing a map showing where they are. These are the zones of mechanical weakness which, when they approach our large cities, are of the first economic importance.

There is also being built in Pasadena, through the courtesy of the California Institute of Technology, a new instrument designed especially for the purpose of studying local tremors and land slips. No such instrument, for the purpose of locating nearby disturbances of this kind, has been devised hitherto. If it proves successful the plan is to establish a number of stations equipped with them, through which to locate very exactly the direction of slips or tremors, and so to know not only the lines of weakness along which such disturbances may be propagated, but also the points of origin from which they may be expected.

You will recall the effort which was made in 1907 by the

California Earthquake Commission, in collaboration with government agencies, to obtain this information after the earthquake of 1906, but the surveys which were then made did not tell us positively either the direction or the magnitude of the displacement which had occurred, because the base-line then chosen was within the zone of the crustal creep, if there was one, and the consequent strain, and therefore within the zone affected by its release. Recognizing these limitations in the earlier effort, it is our hope and purpose not to be found short-sighted again. The astronomers are continuing their observations with additional instruments and, when supported by these surveys of the highest precision, which we hope may be continued for several years, we expect no movement within the coastal plain from Ukiah Observatory to the Mexican boundary to occur without our being able to ascertain precisely its direction, its magnitude, and its probable point of origin. It is my hope that the interest which has been shown by this most influential body in the inauguration of these studies and measurements by the Carnegie Institution of Washington and the scientific bureaus and institutions associated with it, may continue throughout their progress.

To emphasize to you the futility of personal evidence, as opposed to competent instrumental records, it may interest you to know that for a short time I thought to have found precisely the earthquake which I sought. A mining engineer, who was prospecting for values in the vicinity of Lassen Peak during April of 1914, assured me that he both felt and saw a considerable shock from his position a few miles to the east of the mountain, and that this disturbance proceeded visibly in the direction of the volcano crater itself. This direction of progress was also consistent with the general faulting of the region and therefore seemed to fulfil my expectations completely. But I thought best to inquire how he managed to see the earthquake as well as to feel it, and was told that it could be plainly followed by the thin line of dust cloud which marked its progress toward the mountain.

A short time afterward when I happened to meet my old associate in Lassen Peak exploration, Mr. Roy Sifford, who for twenty years has spent at least half of each year at the foot of the mountain, I took advantage of the occasion to ask him what the snow conditions were in the month of April within say twenty miles of Lassen Peak. He replied at once that I could count on from five to six feet of snow at any point within twenty miles of Lassen at that time of the year. Just how it should be possible to observe an advancing dust cloud through six feet of snow was a puzzle which had the immediate effect of discouraging my interest in this particular evidence, and so my hope of completing the chain of circumstances which should explain the inception of volcanic activity at Lassen Peak in 1914 vanished. Perhaps I may yet be successful enough to find a more trustworthy clue. However that may be, this will serve to explain to you why I sought an earthquake in California this summer and the disposition which I proposed to make of it if found.

I thank you for your kind attention.

Manufacture of Vanillin by Electrolysis.—In the spring of 1897, a German patent was issued for a process for producing vanillin by subjecting isoeugenol to an electric current, the vanillin being formed by oxidation and appearing at the anode. The process was described in some detail, consisting essentially in placing in the anode cell a 15 per cent. solution of isoeugenol in an excess of sodium hydroxide, the cathode cell being charged with a 15 per cent. solution of sodium hydroxide. A current of about 5 volts and 6 amperes was recommended. The course of the action is followed from time to time by withdrawing small portions and testing for vanillin. A temperature of about 60° C. is advisable. When the action has progressed well, the anode liquid is shaken with ether which dissolves the vanillin and any unchanged isoeugenol. The vanillin is recovered by shaking with acid sulphite, and this compound decomposed in the usual way.

Notwithstanding the specific claims of this patent, Alexander Lowy and Catherine M. Moore, of the Department of Chemistry, University of Pittsburgh, found by careful experiments that the results stated cannot be obtained. Their work was communicated at the forty-second general meeting of the American Electrochemical Society in September last. All attempts to get an appreciable yield of vanillin failed. Vanillin, itself, was found to oxidize readily, and even if produced in the process will be at once converted into other substances. Experiments were also carried out in which sulphuric acid was used as the electrolyte, but also failed. In all the experiments a resinous substance was obtained. Statements are made in text-books that vanillin can be obtained electrolytically from isoeugenol, but such statements are not borne out by the investigation. If isoeugenol can be so converted, it must be under conditions different from those called for in the patent. H. L.

SCATTERED X-RAYS IN X-RAY PHOTOGRAPHY.*

BY

R. B. WILSEY,

Research Laboratory, Eastman Kodak Company.

When matter is traversed by X-rays, it becomes the source of secondary X-rays. Part of this secondary radiation is of a fluorescent type, of longer wave-length than the exciting rays and, in general, less penetrating. The wave-lengths of the fluorescent radiation have usually been considered to be characteristic of the chemical element emitting them, although Compton [1] has observed evidence of a general fluorescent radiation whose quality is determined by the primary beam of rays and is independent of the material of the radiator. Another part of the secondary radiation consists of scattered rays, whose wave-lengths are the same as those of the primary beam and are independent of the character of the substance emitting them.

In elements of high atomic weight, the secondary radiation consists largely of characteristic rays; in substances of low atomic weight, the characteristic radiation is negligible, the secondary radiation being largely or entirely scattered radiation. Since the human body is composed almost wholly of elements of low atomic weight, it is the scattered type of secondary radiation which is of chief interest in the application of X-rays to the diagnosis and cure of disease.

The present studies were carried out for the purpose of finding the essential facts about scattered radiation as it occurs in making X-ray photographs of the human body, with the object of determining the best method of avoiding its harmful effects upon the quality of the radiograph. The X-ray image is a shadowgraph formed by the primary rays from the focal spot of the X-ray tube; the differences in optical density in the various parts of the radiograph are produced by the differences in absorption of the rays by the various portions of the subject. The scattered radiation reaching the photographic surface diminishes the contrast and detail, rendering the radiograph less valuable for diagnostic purposes.

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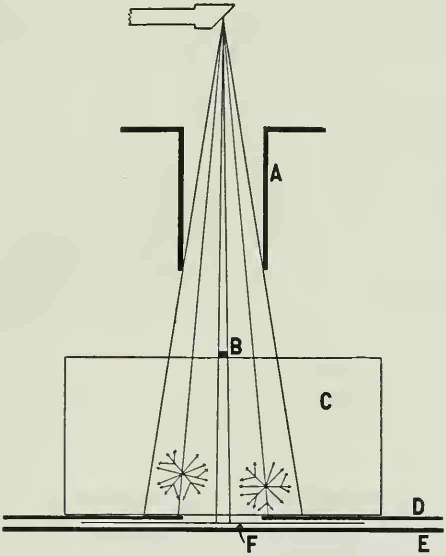
* Communicated by Dr. C. E. K. Mees, Director of the Laboratory and Associate Editor.

Matter is not transparent to X-rays but rather translucent. If the eye were sensitive to X-rays, human tissue when illumined by X-rays would appear to consist of a vapor-like substance. It would resemble more a milky solution than a clear solution. Making an X-ray photograph of a part of the human body is similar to making a photograph of a building through a fog; the parts of the building nearest the camera would appear the most clearly in the photograph and distant portions less clearly or not at all; only the larger outlines would be visible; the finer structural details would be either indistinct or invisible, and the whole photograph would exhibit such lack of contrast and detail as to render it a very unsatisfactory picture. Such is the case with ordinary radiographs of the thicker portions of the human body, and as long as there was no remedy for the effects of scattered rays, we had to be satisfied with such radiographs as could be obtained.

Previous experimental work on X-ray scattering has dealt mainly with the fundamental characteristics of the phenomenon. Only small volumes of scattering material were used in order to minimize extraneous effects such as absorption and rescattering of the scattered rays. The information obtained thus far is very incomplete; some of it is contradictory, and it is not possible to derive from it much knowledge of the behavior of scattered radiation in the relatively large volumes of matter encountered in medical radiography. Accordingly, in the present studies, direct observations were made on the scattered radiation occurring in large volumes of matter under the conditions of practical X-ray photography.

The effect of scattered radiation upon the radiograph depends upon the relative intensity of the scattered radiation and the primary image-forming radiation reaching the photographic film. The method of measuring the relative intensity of scattered and primary radiation is illustrated by Fig. 1. The scattering material *C* consisted of a volume of water contained in an aluminum tank. Water is very similar to human flesh in its absorption and scattering of rays and for that reason was used in nearly all the experiments. A small lead disk *B*, supported over the surface of the scattering material, served to absorb completely all the X-rays striking it so that its shadow on the film could be reached only by the scattered rays and the small amount of primary radiation coming from the portions of the tube outside the focal spot. Since all this radiation is diffuse in character, the radiation falling in the shadow of the lead disk B will be termed *diffuse radiation* while the image-forming radiation received by the film from the focal spot will be called *focal radiation*. The area of the film outside the shadow of the lead disk receives both the diffuse radiation and the focal radiation and it is possible by means of the film F to measure the ratio of the intensity of the diffuse radiation (D) falling in the shadow of the lead disk to that of the total radiation (T) falling outside this shadow.

FIG. 1.



The ratio of diffuse to total radiation, $\frac{D}{T}$, was first measured for various thicknesses of water and for various sizes of image as limited by the lead cylinder A. The Coolidge radiator type tube was operated at 60 kilovolts (effective) and the distance of the target (focal spot) from the film was kept at 20 inches. The tank holding the water was 12 inches square and measurements were made with thicknesses of water varying from 2 to 10 inches. In Table I are given the values obtained when the cone of rays emitted by the tube was sufficient to cover an area 20 inches in diameter in the plane of the film. In column 2 are tabulated the observed values of $\frac{D}{T}$, the ratio of diffuse to total radiation, and in column 3, the values of $\frac{D}{F}$, the ratio of diffuse to focal radiation calculated by the relation

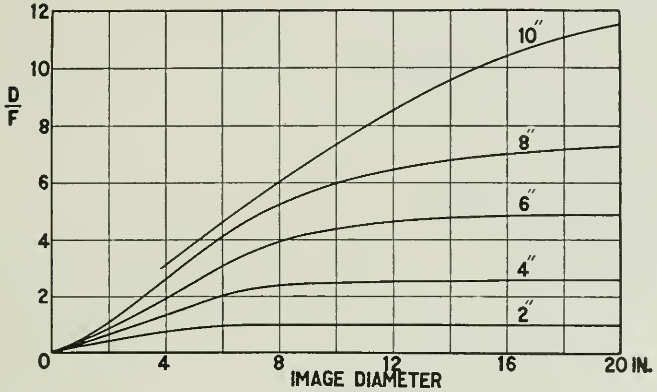
$$\frac{D}{F} = \frac{\frac{D}{T}}{1 - \frac{D}{T}}.$$

Table I.

Thickness of Water in Inches.	Ratio Diffuse to Total Radiation $\frac{D}{T}$.	Ratio Diffuse to Focal Radiation $\frac{D}{F}$.
2	.50	1.0
4	.72	2.6
6	.83	4.9
8	.87	6.7
10	.92	11.5

These values show the important rôle played by scattered radiation in practical radiography. In thicknesses corresponding to the thicker portions of the human body, the diffuse radiation is several times the intensity of the focal radiation which forms the image. These data explain why it is so difficult to get satisfactory radiographs of large patients; the scattered radiation blots out most of the contrast and detail that would otherwise be afforded by the primary rays. It is quite evident that the removal of the scattered radiation would produce a very marked improvement in the quality and diagnostic value of the radiograph. The most common method of reducing the intensity of scattered radiation has been to limit the volume of material rayed by means of a lead cylinder, cone or diaphragm placed between the X-ray tube and the patient. A series of measurements was therefore made to determine the efficiency of this method of removing scattered radiation. The results are shown in graphic form in Fig. 2, which shows the ratio of diffuse to focal radiation plotted against the diameter of the image on the film as determined by the circular diaphragm above the scattering material. The thickness of scattering material (water) is marked on each curve. The ordinate value unity marks the point where the diffuse radiation is equal to the focal radiation; the fact that only a small portion of each curve lies below this value indicates the small range of conditions where the diffuse radiation is reduced to a lower intensity than the focal radiation and, furthermore, to achieve this result, the image must be diaphragmed to a rather small size. This method of reducing the scattered rays does have a limited application in practice; it is sometimes feasible to use a radiograph as small as 4 or 5 inches in diameter, and diaphragming to this size produces an appreciable improvement, although it is not highly efficient in removing scattered radiation.

FIG. 2.



When scattered radiation is removed by any method the exposure must be increased to make up for the loss in total X-ray intensity. The use of a diaphragm between the tube and the scattering material does not affect the intensity of the focal radiation reaching the film; the loss in total intensity is that due to the decrease in scattered radiation and may easily be calculated from the observed ratio of diffuse to total radiation. If the standard exposure for any thickness be taken as that for a twenty-inch image diameter, the factor F by which the exposure must be increased when the image is diaphragmed to a smaller size is given by the equation

$$F = \frac{1 - \frac{D}{T}}{1 - \left(\frac{D}{T}\right)_{20}}$$

where $\frac{D}{T}$ is the ratio of diffuse to total radiation for the image size in question and $\left(\frac{D}{T}\right)_{20}$ is that for an image diameter of twenty inches. Fig. 3 shows the exposure factor as a function of image diameter for the various thicknesses of water.

Decreasing the voltage at which the tube is operated was found to diminish only slightly the proportion of scattered radiation reaching the film.

Another possibility that has been suggested for removing scattered radiation is to insert between the scattering material and the film a filter which absorbs the scattered rays and transmits the primary rays. This suggestion is based upon the supposition that the secondary radiation is of softer or more absorbable type than the primary radiation. The ratio of diffuse to total radiation was therefore measured with several types of filters placed between the scattering material and the film. The results are tabulated in Table II.

Fig. 3.

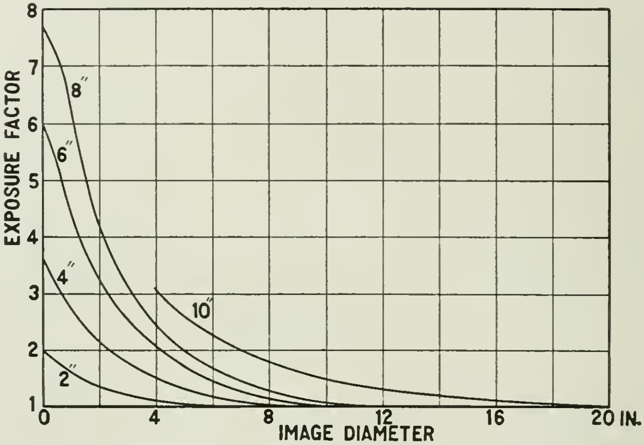


Table II.

Filter.	Ratio Diffuse to Total Radiation.	Ratio Diffuse to Focal Radiation.
None	.83	4.9
1/16-inch aluminum	.82	4.6
1/8-inch aluminum	.80	4.0
.001-inch lead foil	.79	3.8

It is evident that filters are not very efficient in reducing the proportion of scattered radiation. Furthermore, what little advantage they have in this respect is counteracted by their selective absorption of the softer primary rays which give the greatest contrast in the image. Experiments showed that filters used in this way had no measurable effect upon radiographic contrast, their only effect being to increase the exposure.

The enhanced contrast produced by the use of intensifying screens with film has given rise to the suggestion that they owe this effect to a lack of sensitiveness to scattered rays. Measurements were made to determine whether this is the case. The values in Table III show how the proportion of diffuse radiation is recorded by intensifying screens as compared with plain film.

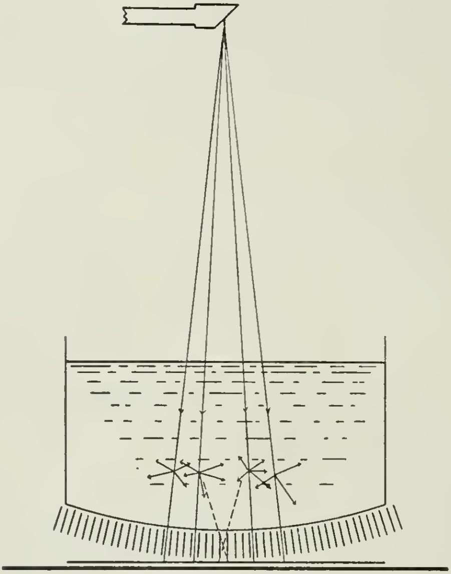
TABLE III.

	Ratio Diffuse to Total Radiation.	Ratio Diffuse to Focal Radiation.
Plain film in cardboard exposure holder.........	.83	4.9
Plain film in aluminum cassette	.81	4.3
Single intensifying screen in aluminum cassette..	.80	4.0
Double intensifying screens in aluminum cassette..	.78	3.5

Measurements on two other types of intensifying screens gave substantially the same results as those above. It is apparent that intensifying screens do not effectively diminish the proportion of scattered rays recorded upon the film.

During the progress of these experiments, a description of the Potter-Bucky diaphragm was published.[2] This apparatus was perfected by Dr. H. E. Potter and consists essentially of a grid placed between the scattering material and the film, so designed as to allow the focal rays to pass through, but absorbing a large portion of the scattered rays. The grid is made of long strips of lead foil, as illustrated in the sectional diagram of Fig. 4. These strips are spaced equal distances apart by intervening wooden strips. The plane of each strip of lead is in line with the focal spot and the long dimension of each strip is parallel to the photographic surface. The focal rays pass through the slots between the lead strips; the scattered rays between a limited angle may pass between the strips; beyond this angle the rays are absorbed by the lead strips. In order to prevent the shadows of the lead strips from showing in the radiograph, the grid is moved continuously during the exposure in a transverse direction perpendicular to the length of the strips while the subject radiographed, supported above the grid, and the film below the grid are kept stationary. The advantage of the Potter-Bucky diaphragm is that its effectiveness does not depend on restricting the size of the radiograph—a radiograph of any size can be made with it—and it is equally efficient in removing scattered radiation over each part of the radiograph. With this diaphragm, Doctor Potter was able to produce radiographs that were far superior in contrast and detail to radiographs made by any other technic.

FIG. 4.



It was decided to make a quantitative study of the Potter-Bucky diaphragm to determine the effect of various factors in design upon its efficiency in removing scattered radiation and in showing fine radiographic detail. Instead of using a complete grid for this study, it was found advantageous to use a single element of the grid, a single slit, formed of thick lead and omitting the wood filling material. A six-inch depth of water in an aluminum tank was used as the scattering material as illustrated in Fig. 4. The X-ray tube was operated at 60 kilovolts and the distance of the focal spot from the slit was kept at 25 inches. The ratio of diffuse to total radiation was measured for various widths and depths of the slit. It was found that the efficiency of the diaphragm in removing scattered radiation depended only on the ratio of the slit width to the slit depth and was independent of the absolute size of the slit. Fig. 5 shows relation between the $\frac{D}{T}$, the ratio of diffuse to total radiation, and $\frac{W_s}{D_s}$, the ratio of the width to the depth of the slit.

FIG. 5.

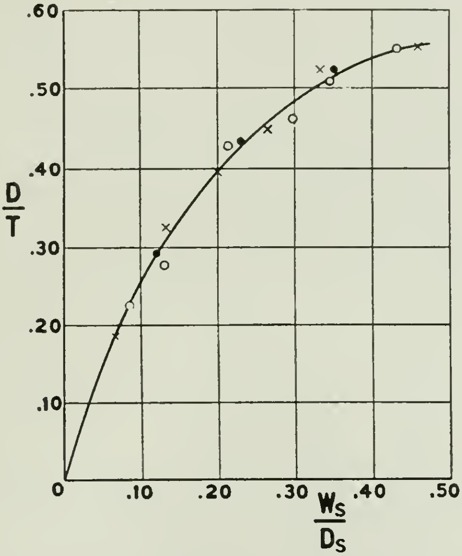


Fig. 6 shows the ratio of diffuse to focal radiation also as a function of $\frac{W_s}{D_s}$.

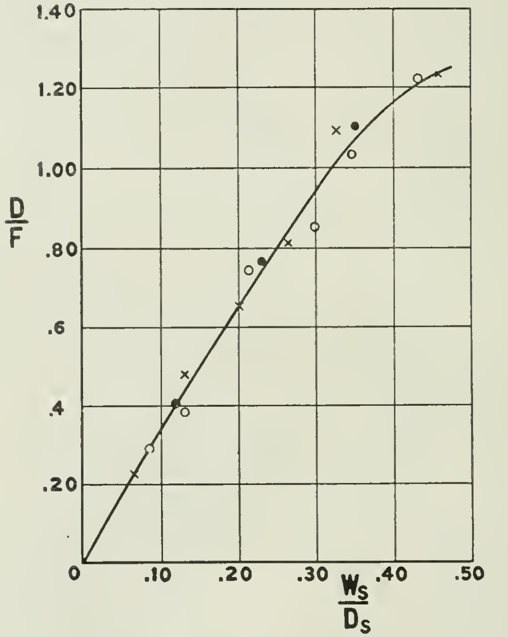
As compared with other methods, it is apparent that the Potter-Bucky diaphragm is highly efficient in removing scattered radiation. For instance, in a six-inch depth of water, a Potter-Bucky diaphragm with a slit ratio, $\frac{W_s}{D_s}$, of 0.2 is as effective in removing scattered radiation as a circular diaphragm above the water giving an image diameter of 1.5 inches, and the Potter-Bucky diaphragm cleans up the scattered radiation with equal effectiveness over the whole area of a full-size radiograph.

If we define the efficiency of a diaphragm as the fraction of the scattered radiation removed by it, for a six-inch depth of water the efficiency may be calculated from value of $\frac{D}{F}$ by the equation

$$E = \frac{4.9 - \frac{D}{F}}{4.9}.$$

Fig. 7 shows the efficiency of the Potter-Bucky diaphragm as a function of the slit ratio, $\frac{W_s}{D_s}$. Slit ratios of 0.25 to 0.17 or less are entirely practicable and give efficiencies ranging between 80 and 90 per cent.

FIG. 6.

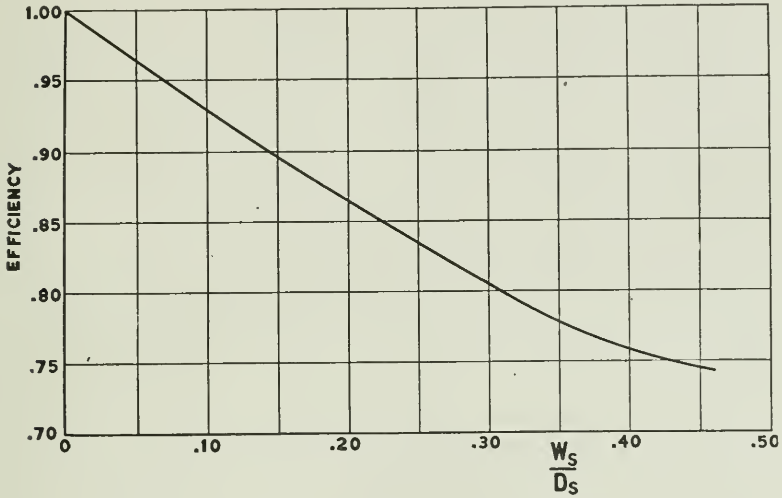


The exposure factor of the Potter-Bucky diaphragm is shown as a function of the slit ratio in Fig. 8.

In a practical Bucky grid, the strips of lead foil are held apart in their proper positions by strips of wood. Measurements showed that the effect of these wooden strips upon the efficiency is almost negligible. The lead strips transmit some of the scattered rays incident upon them and this factor also lowers slightly the efficiency in a complete grid. The exact effect of the transmission of scattered rays by the lead strips has not been determined but preliminary experiments indicate that the effect is not large.

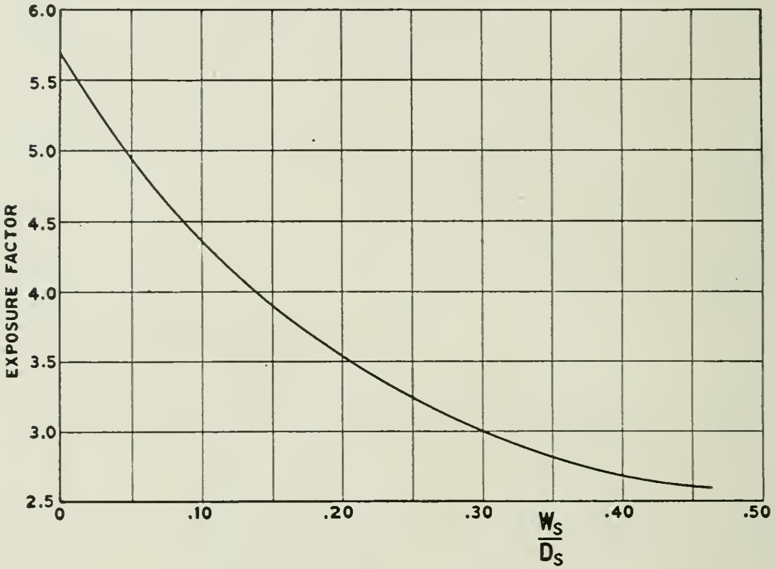
The effect of the Potter-Bucky diaphragm in enhancing contrast in the radiograph depends upon the efficiency in removing scattered radiation. The definition in the radiograph is affected by an additional factor, the increased distance between the patient and the film necessitated by this diaphragm. It is to be expected that this increase in distance will, to some extent, counteract the beneficial effect of removing scattered radiation upon definition. This was found to be the case. The definition obtainable in radiographing through a scattering material was studied by means of a set of wire gauzes of various sized meshes immersed in the tank of water. The distance between the scattering material and the film was found to have a very marked effect upon the radiographic definition. If the distance between scattering material and film were too great, the definition was better without the diaphragm than with it. It was also found, for instance, that if the slit width were kept at a constant value of, say, 0.13 inch, and the slit depth diminished from 1.00 inch to 0.20 inch to permit a shorter distance between scattering material and

FIG. 7.



film, the definition was improved, although this procedure allowed more scattered radiation to fall on the film. With a six-inch depth of water and a distance of 0.7 inch between the water and the film, a slit ratio of 0.26 gave the same definition as was obtained without the diaphragm. Either a smaller slit ratio or a lesser distance between scattering material and film was required to gain an improvement in definition. When the distance between scattering material and film was as large as one inch, the smallest slit ratio tried, 0.044, failed to give as good definition as was obtained without the use of any diaphragm. The advantage of the ordinary technic without the diaphragm in this case is that the subject radiographed is very close to the film. If, however, with the Potter-Bucky diaphragm the distance between scattering material and film is made sufficiently small, a marked improvement in definition is produced. To obtain high contrast as well, the ratio of slit width to slit depth should be small. The problem in grid design, then, is to make the grid as thin and fine-meshed as possible. Some clear space must be allowed above and below the grid to allow it to travel free from any friction caused by rubbing against the cassette containing the

Fig. 8.



film or the cover supporting the patient. This clear space should be reduced to a minimum and the thickness of the top of the cassette and the thickness of the cover of the diaphragm should also be made as small as possible, so that every precaution is taken to minimize the distance between patient and film.

As will be noted from Fig. 4, the grid has a curvature like the surface of a cylinder. If the film is held flat, the distance between scattering material and film is greater at the edge of the film than at the centre. In order to obtain the same excellence of definition over the whole area of the film, the curvature of the film should follow that of the grid, keeping the same distance between scattering material and film over its whole area. The use of a curved cassette for holding the film has been suggested by Van Allen,[3] who finds that it reduces both the distortion and fuzzy appearance (poor definition) which are characteristic of objects distant from the film.

It is often suggested that an additional improvement in the Potter-Bucky diaphragm would be obtained if the lead strips extended in both directions, forming a set of rectangular cells. The cellular grid is the design generally ascribed to Bucky's original invention. Experiments on the definition obtainable with small rectangular cells showed that for equal distances between patient and film and equal ratios of width to depth, the cells gave but little better definition than was obtained by the long slit. If it were possible to construct economically a cellular type of grid, so designed that it could be moved during the exposure as to avoid grid shadows upon the film, it would doubtless be of advantage. Other types of grid are readily conceivable, such as a flat grid with radial slits, or with one continuous lead strip bent in the form of a spiral. These could be rotated to avoid grid shadows instead of requiring a transverse motion. The trouble with such designs would be the difficulty and cost of construction which would scarcely be justified by the slight improvement they would afford. The present experiments indicate that the most practicable procedure is to push the Potter type of grid to the limit of its effectiveness.

To try out in a practical way the conclusions reached in this study of the Bucky diaphragm principle, a thin, fine-meshed grid was constructed. The grid was made 0.16 inch thick; lead-foil strips three-thousandths of an inch thick were spaced at a distance of .026 inch apart by means of strips of celluloid. The curved frame in which the grid was mounted was fitted with an aluminum floor 0.02 inch thick to support the grid over its whole area. Some difficulty was experienced in getting the lead strips lined up properly, but after some adjustments a fairly satisfactory result was obtained. The cover of the diaphragm for support of the patient was of 1/32-inch aluminum mounted on a curved frame and the top of the curved cassette was also of 1/32-inch aluminum. When sufficient space was allowed for the grid to travel without friction, the total distance from the patient to film was found to be 3/8 inch. Probably by additional adjustments, this distance could be reduced slightly. In present commercial models of the Potter-Bucky diaphragm, the distance between patient and film ranges from 3/4 inch to 1 1/4 inches, and they are designed to take flat cassettes. Radiographs of several portions of the body showed clearly the advantage of the experimental diaphragm over the usual type of diaphragm in radiographic definition. The advantage of this diaphragm in giving sharpness of outline and fine structural detail was especially noticeable at the edge of the film where the curved cassette brings the film much closer to the patient than does the flat cassette employed with present commercial diaphragms.

Although there is still some room for improvement, the Potter-Bucky diaphragm in its most efficient form may be considered a very satisfactory solution of the problem of scattered radiation in radiography. Radiographs made with the diaphragm show a striking superiority in both contrast and detail over those made by the ordinary methods. The only disadvantage is the increased exposure required, necessitating increased precautions for immobilizing the part rayed and permitting fewer radiographs to be taken with safety to the patient. This disadvantage is inherent in any method of removing scattered radiation and the more scattered rays are removed, the greater must be the exposure required to compensate for the loss in total X-ray intensity.

REFERENCES.

[1] Compton, A. H.: *Phys. Rev.*, **18**, p. 96, Aug., 1921.
[2] Potter, H. E.: *Am. J. Roentgenol.*, 7, June, 1920, p. 292.
[3] Van Allen, H. W.: *Am. J. Roentgenol.*, **8**, June, 1921, p. 340.

THEORY OF END-LOSS CORRECTIONS AND ITS APPLICATION TO UNIFORM, ELECTRICALLY HEATED TUNGSTEN FILAMENTS IN VACUO.*

BY

A. G. WORTHING, Ph.D.

Laboratory of Pure Science, Nela Research Laboratories.

INTRODUCTION.

With the advent of metal filament, incandescent lamps, the existence of losses where the filaments are attached to lead-wires or come in contact with supports, became a matter of concern. The magnitudes of these end-losses, as they are called, were studied [1, 2] and means for reducing them as far as practicable were considered and employed.

The commercial investigation consisted of an adaptation of the optical pyrometry methods of pure science to the study of small incandescent filaments. In addition to yielding results of importance in lamp design, that work led to a broader study of materials at high temperatures from the viewpoint of pure science. In fact, the physical properties of many materials are studied with ease only in case they may be mounted in filament form and heated electrically. To obtain results in such cases applicable to uniformly heated portions of the material, consideration must be given to the end-losses resulting from the conduction of heat from the filament to the leads and supports.

End-loss effects may be eliminated (1) by selecting filaments that are so long that the corrections are negligible; (2) by taking difference measurements on filaments differing only in length; (3) by determining the corrections to be applied through a study of the variation in temperature and related properties near a cooling lead or support, or (4) by introducing devices which permit of measurements on uniformly heated portions of the filaments only. The device will depend upon the problem. In electrical measurements, small potential leads attached to the main filament at considerable distances from the cooling leads may be used; in thermionic measurements, a cylindrical anode about the central portion of the filament, slightly separated from two others of the same diameter about the end portions, will serve.

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* Communicated by the Director of the Laboratory.

In much work, computed end-loss corrections serve as satisfactory approximations. In fact, in case of initial imperfection or of accident occurring during the course of the work, computation may prove the only means of salvaging data and results obtained on materials originally mounted for study by methods (1) or (2). Moreover, once the corrections are determined accurately, this procedure may result in saving much time, for actual end-loss determinations are usually not simple.

TABLE I.

Quantities and Symbols.

Symbol.	Quantity.
T	temperature.
i	filament current density.
ρ	resistivity.
σ	radiation intensity.
k	thermal conductivity.
r	filament radius.
l	distance along filament from junction.
b	filament brightness.
e	thermionic current density.
sub m	values occurring at centre of a long filament.
sub μ	values occurring at centre of short filament.
sub j	values occurring at junction of the filament with support or lead.
sub o	values corresponding to a "standard" operating condition in which $r = .01$ cm. and $T_m = 2400°$ K.
$\alpha \quad \frac{T}{\sigma}\frac{d\sigma}{dT}$	ratio of percentage change in σ to corresponding percentage change in T.
$\beta \quad \frac{T}{\rho}\frac{d\rho}{dT}$	ratio of percentage change in ρ to corresponding percentage change in T.
$\delta \quad \frac{T}{b}\frac{db}{dT}$	ratio of percentage change in b to corresponding percentage change in T.
τ	T/T_m, reduced temperature.
$Q \quad \sqrt{\frac{2\sigma_m(\alpha-\beta)}{k_m T_m}}$	
P	Q/r, factor for obtaining reduced distributions.
L	Pl, reduced length.
w	width of filament.
t	thickness of ribbon filament.
Δl	effective filament shortening due to end loss.

This paper contains a method for computing end-loss corrections and an application of it to the case of uniform, electrically heated, tungsten filaments in vacuo.

As previous work not already mentioned which serves as a foundation for the present paper, reference should be made to Worthing,[3, 4, 5] Langmuir,[6] and Stead.[7]

THE LONG FILAMENT.

Theory.—A long filament for this purpose is defined as one in which the cooling effects due to the leads or supports do not appreciably affect the temperature of the central portion. In contrast to the short filament, discussed later, the cooling effect at any point in a long filament is due only to a single lead or support.

Consider a long, uniform, electrically heated, cylindrical wire in vacuo, whose variations in resistivity, thermal conductivity, and radiation intensity with temperature are known. Assume the temperature variation over any cross-section so small that the surface values of the resistivity, etc., at any point may be taken without appreciable error as the average over the cross-section. In the ordinary metallic filaments used in lamps, this is closely realized. How closely this is the case is shown by the fact that in a 0.2 mm. tungsten filament, approximately that of the 500-watt, 110-volt tungsten lamp used previous to the advent of the gas-filled lamp, the greatest difference in temperature between axis and surface normally did not exceed a quarter of a degree.[3]

The fundamental equation giving, on the above assumptions, the temperature distribution near a cooling lead (see Table I) is

$$\text{(1)} \quad i^2\rho\pi r^2 dl + \left[k\frac{d^2T}{dl} + \frac{dk}{dT}\left(\frac{dT}{dl}\right)^2\right]\pi r^2 dl = 2\pi r\sigma dl.$$

The three terms in order represent, for an element of filament of length, dl, the rate of production of heat electrically within it, the net rate of conduction of heat into it through its ends, and the rate of radiation of energy from its cylindrical surface.

Equation 1, with conditions characteristic of long filaments introduced, leads finally to a form which may be evaluated to give the variation in temperature along the filament. Throughout a considerable part of the end-cooled length, the evaluation is best done graphically or algebraically. However, in the region where the temperature T is nearly equal to the central maximum temperature T_m, accuracy and ease of evaluation are brought about by the close approach to the well-known exponential form for the temperature distance relation, in which

$$(2)\quad \left[\frac{dT}{dl} = \frac{Q}{\sqrt{r}}(T_m - T) = P(T_m - T)\right]_{T \underset{\cdot}{=} T_m}$$

or expressed integrally

$$(3)\quad \left[1 - \frac{T}{T_m} = e^{-P(l-l')}\right]_{T \underset{\cdot}{=} T_m}$$

Q is a combined function of several properties of the filament material each of which is a function of T_m only, r is the filament radius, l' an integration constant, and P a convenient abbreviation for $Q/\sqrt{r}$.

Once the curve giving the temperature variation in an end-cooled portion of a filament is platted, other curves giving resistivity, etc., variations may be obtained through their known dependencies on temperature.

For much that follows it is convenient to rewrite (2) and (3) in reduced forms in which T/T_m is replaced by τ and Pl by L. Thus

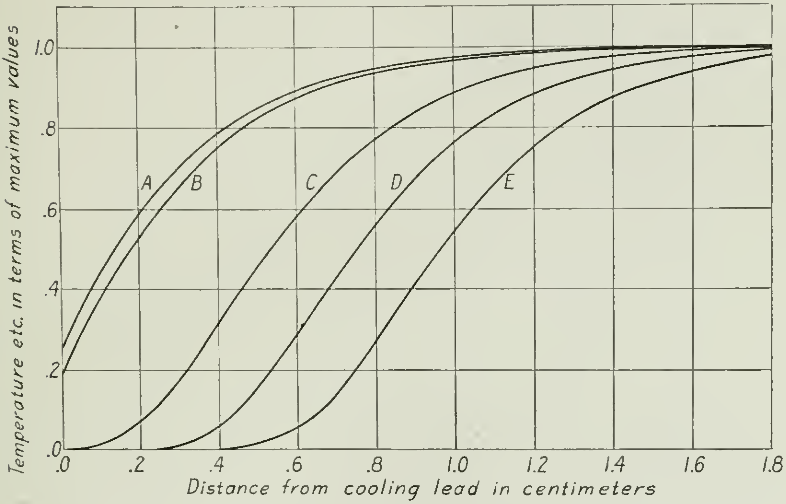
$$(4)\quad \left[\frac{d\tau}{dl} = P(1-\tau)\right]_{\tau \underset{\cdot}{=} 1}$$

$$(5)\quad \left[1 - \tau = e^{-P(l-l')} = e^{-(L-L')}\right]_{\tau \underset{\cdot}{=} 1}$$

in which τ and L may be conveniently called reduced temperature and reduced length. Equation 5 gives the important generalization that *all end-loss curves in reduced units showing temperature variation with distance for a given substance are identical in the region where T approximates T_m*, that is, where τ approximates unity. The unit of τ is the central maximum temperature, the unit of L that distance along the filament where (5) applies, through which $1 - \tau$ decreases to $1/e$ th of the value possessed at the beginning of the length interval. P is to be considered a transformation factor whereby lengths in ordinary units may be transformed into reduced units and *vice versa*. The ratio of two P's, when the end-loss curve giving the temperature variation corresponding to one of them is known, may evidently be used in accord with (4) to determine the temperature variation for the other in the region where T approximates T_m.

Distribution Curves for Long, Electrically-heated Tungsten Filaments in Vacuo.—The data used as a basis for computing distribution curves for tungsten consist of a temperature scale,[8] the thermal conductivity,[8] the resistivity, and the radiation intensity functions[9] of temperature obtained by combining a determination of the brightness of a black body,[10] together with emissive powers and the deviation of the emission of tungsten from Lambert's cosine law[11] and results on thermionic emission.[12] The thermal conductivity data are the least satisfactory of all.

FIG. 1.



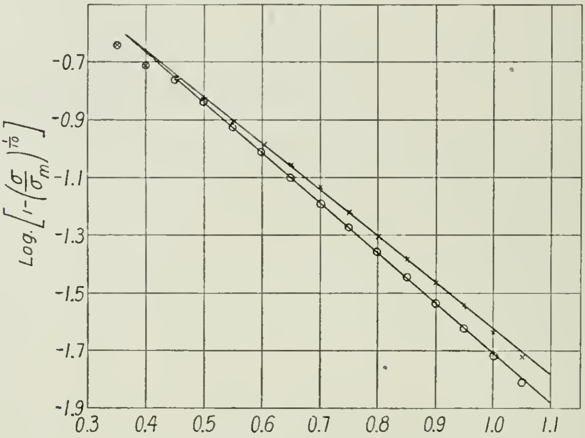
Various distribution curves for a long tungsten wire ($r = 0.01$ cm.) electrically heated in vacuo to a central maximum temperature of 2400° K. *A*, Temperature; *B*, Resistivity; *C*, Radiation intensity; *D*, Brightness; *E*, Thermionic emission intensity.

Curve *A*, Fig. 1, shows the temperature distribution for the particular case of a long tungsten filament having a diameter of 0.2 mm. electrically heated to a maximum temperature of 2400° K. The other distributions shown follow simply as stated from their known functions of temperature. Curve *C* was found to check exactly[4] with data published previously, giving σ as a function of l in a particular case.

It is a curious fact that, to a large extent, any one curve of Fig. 1 can be obtained by shifting any other curve laterally and without distortion by a fixed amount. Thus starting with the thermionic output curve *E*, successive shifts to the left of 0.22 cm., 0.43 cm., 0.78 cm., and 0.82 cm. give in succession the approximate positions of curves, *D, C, B,* and *A*.

The deviations of curve *A*, Fig. 1, from the form given by (3) in the region where T is considerably less than T_m, are not great. Moreover, a comparison of various computed curves corresponding to a considerable range of T_m showed these deviations to be always the same in direction and approximately the same in magnitude, and indicated that the generalization regarding the identity of reduced distributions for the region where T approximates T_m might also apply outside this region in the case of tungsten. The broader application to include both regions requires further inquiry into its significance and its correctness. In a more specific way it states that, for any given value of τ $(=T/T_m)$, the temperature gradient dT/dl must vary as P. For test purpose, there are two independent phases corresponding to the two independent variables of which P is a function. One involves a variation in r, the other in T_m. Thus for filaments having different radii, but the same central operating temperature T_m, dT/dl must vary as $1/\sqrt{r}$, while for a given filament with various T_m values, dT/dl must vary as the corresponding Q's.

FIG. 2.



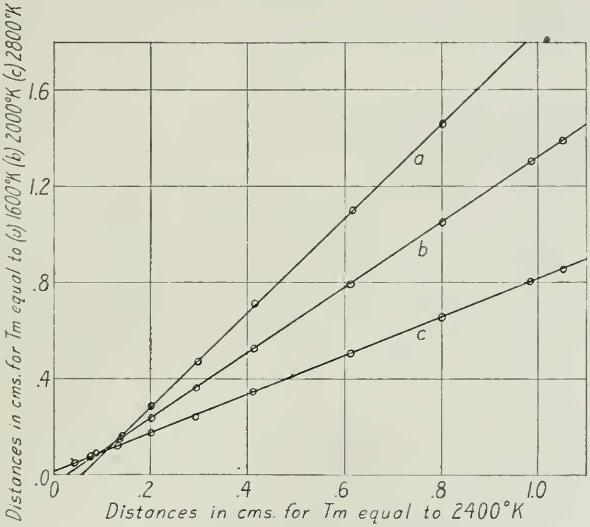
Distance along the filament in centimetres.

The radiation intensity distribution for a particular tungsten filament ($r = 0.01045$ cm.) heated to a maximum temperature of 2475° K. (1) by a current of 4.32 amps. directed away from the cooling junction (⊙⊙⊙), and (2) by a current of the same intensity directed toward the cooling junction (xxx).

The first phase relating to varying radii is theoretically exact, and the experimental test generally verified the prediction, though with a considerable range of uncertainty which may well be ascribed, among other things, to differences in filament manufacture and grain structure.

The second phase is theoretically inexact; but, due to being carried out wholly on a single filament, the test showed a much better verification. For a range of T_m values extending from 1976° K to 2667° K (the greatest range for which the writer has obtained distribution on a single filament in his past work), corresponding values of dT/dl were found to agree to within one or two per cent. This is based on a comparison of the slopes of the lines obtained when, as in Fig. 2, the empirical functions of radiation intensity $\log\left[1-\left(\frac{\sigma}{\sigma m}\right)^{1/10}\right]$ were platted against distances from the junction with the lead.

FIG. 3.



Distances from a cooling lead in a long tungsten wire filament (r = 0.01cm.) heated electrically in vacuo to various central maximum temperatures T_m as a function of distances to corresponding temperatures when the maximum is 2400° K.

To see whether existing data are consistent with the varying T_m phase throughout a more extended range, computed distributions for such an extended range were compared. From additional curves similar to curve A of Fig. 1, corresponding to T_m values of 2800° K, 2000° K, and 1600° K, values of l corresponding to arbitrarily chosen values of T were platted against the l's for the same values of T from the 2400° K curve (see

Fig. 3). The points lie on straight lines whose slopes 0.80, 1.34, and 1.95 are quite closely given by the calculated ratios Q_0/Q (see Table II), namely 0.80, 1.32, and 1.91. Though the agreement is not exact, it is such as to indicate the substantial correctness of this phase.

As a close approximation, all end-loss temperature distribution curves for tungsten, platted in reduced units, are identical throughout.

Reasoning and tests similar to the foregoing show that similar conclusions concerning the end-loss resistivity, brightness, etc., distributions hold with approximately the same accuracy. The transformation factor whereby length in ordinary units may be expressed in reduced units and *vice versa* is in each instance P, as in the temperature case. For example, in the case of filament brightness, b, the equation analogous to (3), is

TABLE II.

Data on Tungsten Useful in the Application of (2) to (6) and in the Determination of Unknown Distributions from a Standard Set on the Basis of Identical "reduced distribution" Curves.

T °K	σ $\frac{\text{watts}}{\text{cm.}}$	$\alpha = \frac{T}{\sigma}\frac{d\sigma}{dT}$	ρ ohm cm.	$\beta = \frac{T}{\rho}\frac{d\rho}{dT}$	k $\frac{\text{watts}}{\text{cm. deg.}}$	$\frac{T}{k}\frac{dk}{dT}$	b $\frac{\text{candles}}{\text{cm.}^2}$	$\frac{T}{b}\frac{db}{dT}$	$\frac{T}{e}\frac{de}{dT}$	Q cm.$^{-1/2}$
2800°K	117.5	4.53	0.0_4887	1.20	1.27	0.4	688.	8.88	20.3	.470
2400	57.7	4.68	737	1.20	1.19	0.4	156.	10.3	23.6	.375
2000	24.2	4.87	592	1.20	1.11	0.4	20.0	12.3	28.2	.2835
1600	7.88	5.17	453	1.20	1.01	0.4	0.96	15.0	35.1	.1965
1200	.166	5.60	321	1.20	0.90	0.4	......	.....	....	.116

$$(6)\quad \left[1 - \frac{b}{b_m} = e^{-P(l-l')}\right]_{b = b_m}.$$

The l' in this case differs from the l' of the temperature case by approximately the latteral shift which is necessary, as has been noted in discussing Fig. 1, to bring the two corresponding curves into practical coincidence.

Given curve *A*, Fig. 1, and the data of Table II, suppose the temperature distribution curve for a long tungsten filament 0.25 mm. in diameter with a maximum temperature of 2800° K is wanted. Representing by subscript 0 values referring to 2400° K, we have then for the transforming factor P/P_0, as shown by (4),

$$(7)\quad \frac{P}{P_o} = \frac{d\tau}{dl} \div \left(\frac{d\tau}{dl}\right)_o = \frac{Q}{Q_o}\sqrt{\frac{r}{r}} = 1.122.$$

The 2800° K temperature distribution is therefore obtained by shortening all distance measurements on curve *A*, Fig. 1, by the factor 1.122. This distribution, it should be emphasized, is that obtained with an alternating current or the average of those obtained at the two ends of a filament heated by a direct current. For the convenience of others, a group of values for P/P_0 are given in Table III.

TABLE III.

Values of P/P_0 for Use in Conjunction with Equation 7 and Fig. 1 in Determining Distributions Corresponding to Various Filament Radii r and Central Maximum Temperatures T_m, and of P for Use in Conjunction with Equations 8 to 12 in Determining Effective Filament Shortenings, $\triangle l_A$, etc.

T_m in °K	r in cm.	0.001	0.002	0.005	0.010	0.015	0.020	0.030
1000	$P/P_0 =$	.670	.472	.298	.211	.172	.149	.122
	$P =$	2.50	1.76	1.12	0.79	0.645	0.56	0.46
1200	$P/P_0 =$	.980	.690	.437	.309	.252	.218	.178
	$P =$	3.65	2.60	1.64	1.160	.945	.820	.670
1400	$P/P_0 =$	1.315	.930	.588	.416	.339	.294	.240
	$P =$	4.95	3.50	2.21	1.560	1.275	1.105	.900
1600	$P/P_0 =$	1.650	1.120	.740	.523	.427	.370	.302
	$P =$	6.20	4.38	2.77	1.965	1.605	1.390	1.135
1800	$P/P_0 =$	2.01	1.420	.898	.635	.518	.449	.366
	$P =$	7.55	5.32	3.36	2.38	1.940	1.680	1.375
2000	$P/P_0 =$	2.40	1.695	1.070	.758	.618	.536	.438
	$P =$	9.00	6.35	4.02	2.84	2.32	2.01	1.640
2200	$P/P_0 =$	2.777	1.955	1.235	.875	.714	.618	.505
	$P =$	11.35	7.35	4.64	3.28	2.68	2.32	1.895
2400	$P/P_0 =$	3.16	2.24	1.415	1.000	.816	.707	.578
	$P =$	11.85	8.40	5.30	3.75	3.06	2.65	2.16
2600	$P/P_0 =$	3.56	2.52	1.590	1.125	.918	.796	.650
	$P =$	13.35	9.45	5.96	4.22	3.45	2.98	2.44
2800	$P/P_0 =$	3.96	2.80	1.775	1.254	1.024	.887	.724
	$P =$	14.85	10.50	6.65	4.70	3.84	3.32	2.71
3000	$P/P_0 =$	4.38	3.10	1.960	1.385	1.130	.980	.800
	$P =$	16.40	11.60	7.35	5.19	4.23	3.67	3.00

Granted the foregoing conclusions, the development of general expressions for integral end-losses is much simplified. Without question, for end-loss correction purposes, errors made by assuming the identity of the reduced distributions are less than other experimental uncertainties.

End-loss Corrections.—An end-loss may be most satisfactorily viewed as an effective filament shortening. Referring to Fig. 1, curve *D*, it is easily seen that, from a light production standpoint, the filament is effectively about 0.8 cm. shorter than it would be were the filament uniformly bright all the way to the lead. The effective length of the filament is thus shortened by about 0.8 cm. Similarly, from the thermionic emission standpoint, the effective filament shortening is about 1.0 cm., etc. The exact shortening in any case will depend on the temperature T_j at the junction of filament to the lead or support.

For most purposes only rough estimates of T_j are necessary. In illustration, compare the temperature distribution of Fig. 1 in which T_j equals 600° K with that for the same filament operated at the same T_m but with T_j equal to 800° K. Evidently the part of the filament between 600° K and 800° K for the first case bears the same relation to the portion beyond the 800° K point that the junction in the second case bears to the filament as a whole; and hence, beyond the 800° K points, the distributions are identical. Referring to Fig. 1, it will be seen that the two cases differ in effective shortenings by about 0.04 cm. Unless otherwise stated, in this paper T_j is assumed to be $T_m/4$.

On the basis of identical reduced distributions, each of the effective shortenings varies as $1/P$. Representing by Δl_A, Δl_B etc., in accord with the lettering of the curves of Fig. 1, the effective filament shortenings at a single junction from the standpoint of heat content, resistivity or energy input, radiation output, light emission, and thermionic emission; and evaluating proportionality constants from the plat, we obtain the following simple end-loss expressions, giving values in cm.

$$(8) \quad \Delta l_A = 0.88 \sqrt{r}/Q = 0.88\, 1/P \text{ (heat content)}$$

$$(9) \quad \Delta l_B = 1.00 \sqrt{r}/Q = 1.00\, 1/P \text{ (energy input)}$$

$$(10) \quad \Delta l_C = 2.25 \sqrt{r}/Q = 2.25\, 1/P \text{ (radiation output)}$$

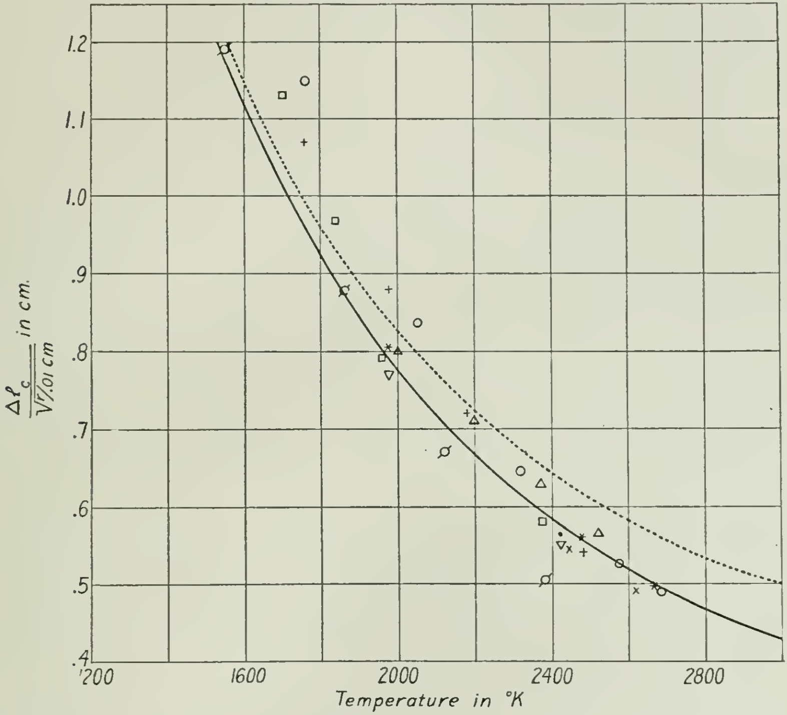
$$(11) \quad \Delta l_D = 3.00 \sqrt{r}/Q = 3.00\, 1/P \text{ (light emission)}$$

$$(12) \quad \Delta l_E = 3.85 \sqrt{r}/Q = 3.85\, 1/P \text{ (thermionic emission)}$$

To apply these equations it is necessary to know r and T_m. Once T_m or r is known; the others may be determined from wattage and resistance considerations.[9]

Equations 8 to 12 indicate that, other things unchanged, the effective filament shortenings vary as $\sqrt{r}$. The variation in total filament length with radius for vacuum lamps operating at the same voltage and temperature follows the same law. Hence, other things unchanged, the percentage end-losses for lamps of different wattage but the same voltage and the same temperature of operation are the same. The percentage end-loss in a 10-watt, 115-volt lamp, is the same as that in a 100-watt, 115-volt lamp.

FIG. 4.



Observed effective filament shortenings due to a single cooling junction from the radiation output standpoint $\triangle l_{c,}$ for various sized tungsten filaments (00025 cm· $<r<$ 0.013 cm.) reduced to give expected shortenings for a filament having a radius of 0.01 cm., platted as a function of the maximum temperature, T_m. The full line represents calculated values for the case $T_j = T_m$, the dashed line values for the case $T_j = 300°$ K.

4

A test of any one of equations 8 to 12 is a test of all, since all of the physical properties are definite functions of the same independent variable, T. Selecting 10 as convenient, data previously obtained have been gone over and wherever possible determinations of Δl_C computed. In Fig. 4, these have been platted as functions of T_m. The full line represents equation 10. Considering possible variations in T_j due to difference in lamp construction, in crystal structure resulting from changes in lamp manufacture and from differential temperature treatment in any single filament during previous operation, and in filament diameter resulting from vaporization during previous operation, the agreement between observed and computed values is not bad. The dashed line of Fig. 4 gives what might be expected if equation 10 were corrected for a common T_j or 300° K.

Some indications of the energy input and light output end-losses for commercial lamps are of interest. The ordinary 40-watt, 115-volt vacuum tungsten lamp with a filament 51 cm. long and 0.038 mm. in diameter has two large copper leads and eleven small molybdenum hook supports. T_m is about 2450° K. The lead junctions are of such size that T_j lies between $T_m/4$ and $T_m/3$. T_j for the smaller molybdenum hooks is much larger about 1750° K. Because of this high value, equations 8 to 12 are not applicable here. However, on the basis of identical reduced distributions, the end-loss for any described condition is not difficult to obtain by graphical integration using Fig. 1. Doing this and taking account of the fact that at the hooks the cooling extends both forward and backward, the total effective shortenings in the lamp have been determined. From the energy input and the light output standpoints they amount to about 1.1 cms. and 5.2 cms., that is, to about 2.2 per cent. and 10 per cent. Whence the end-loss results in a decrease in luminous efficiency of 7.8 per cent.

For most purposes, the end-losses in long filaments, whatever the values of r and T_m, may be computed with considerable precision with the aid of equations 8 to 12.

THE SHORT FILAMENT.

The short filament for this purpose is defined as one in which the cooling effects due to the leads or supports appreciably affect the temperature of the central portion. In contrast to the long filament, the total cooling effect at some points at least are due to two separate leads or supports.

In the long filament in vacuo near the centre of its length, the rate of production of heat in any element of length is equal to the rate of radiation of energy from its surface. In the short filament this equality does not hold; there is always a net rate of transfer of heat by conduction out from the ends of the element of length toward one of the leads or supports. It is this characteristic difference which results in the differences in the end-loss curves for the two kinds of filaments.

Equation 1, with conditions characteristic of short filaments, introduced leads to an expression which shows well the similarity and the difference which short filament distributions bear to long filament distributions. It is

$$(13)\quad \underset{\substack{T\\ \text{short}}}{\left(\frac{dT}{dl}\right)^2} = \underset{\substack{T\\ \text{long}}}{\left(\frac{dT}{dl}\right)^2} - \underset{\substack{T_\mu\\ \text{long}}}{\left(\frac{dT}{dl}\right)^2}$$

in which by the double subscript the temperature and the type of filament are specified. In illustration, consider two filaments of the same cross-section, one long and the other short, which are heated by the same current to central maximum temperatures $T_m = 2400°$ K and $T_\mu = 2000°$ K, respectively. Then $\left(\frac{dT}{dl}\right)^2$ for the short filament at the point where $T = 1800°$ K, say, is equal to $\left(\frac{dT}{dl}\right)^2$ for the long filament at 1800° K less $\left(\frac{dT}{dl}\right)^2$ for the long filament at 2000° K. In a plat of $\left(\frac{dT}{dl}\right)^2 = f(T)$ the curve for the short filament is obtained by shifting the curve for the long filament perpendicular to the T axis until it intersects at 2000° K. This condition greatly simplifies the treatment of short filaments, which also may be shown to follow the reduced distribution principle. Any desired distribution may be obtained from a standard set.

A standard set of distribution curves for various short tungsten filaments 0.2 mm. in diameter, together with the method for using them and the results of tests, will be published in a fuller discussion elsewhere.

THE RIBBON FILAMENT.

Assuming identical properties for the filament materials, it follows that end-losses for ribbon filaments are related simply to those for cylindrical or wire filaments. The fundamental end-loss equation differs from (1) by the substitution of the expressions for the cross-sectional area wt and the perimeter $2\ (w+t)$

of the ribbon for the analogous wire expressions πr^2 and $2\pi r$. Further equations and theory are modified only by the substitution of $(1/w + 1/t)$ for $1/r$, *e.g.*,

$$(14) \quad P = Q\left(\frac{1}{w} + \frac{1}{t}\right).$$

The reduced distribution curves for ribbon are identical with those for wire filaments, both long and short. The effective shortenings are identical when for the same T_m or T_μ $(1/w + 1/t)$ equals $1/r$.

In equivalent wire and ribbon filaments (that is in filaments having the same resistance and the same wattage for the same T_m) operated at the same T_m, the percentage end-losses are equal.

The above conclusions were tested in a comparison of a wire filament 3 cm. long and about 0.12 mm. in diameter with a ribbon filament 2 cm. long and an approximate cross-section of .029 mm. × .25 mm. Allowing for the small deviation from equivalence, the two lamps were found, when operated at the same temperatures, to have the same luminous efficiency to well within the uncertainties of measurements, though the reductions due to the ends were of the order of 30 per cent.

Reasoning similar to the above shows that, whatever the cross-section of the filament, the end-loss expressions may be obtained by substituting the ratio of its cross-section to its perimeter for $r/2$ in the corresponding expressions for wire filament.

SUMMARY.

The Long Filament.—General expressions for the temperature, resistivity, emission intensity, brightness, and thermionic emission distributions near a cooling junction, for uniform electrically heated filaments mounted in vacuo, have been derived. Those computed for tungsten were found to check observed distributions closely. It was found that, for each type of distribution curves, there is a single reduced distribution from which by means of a simple theoretical transformation factor P (see Table I) any desired distribution may be obtained with considerable exactness. It follows that the various effective filament shortenings from different standpoints, *i.e.*, the effective measures of end-losses, vary inversely as the transformation factor P (equations 8 to 12).

The Short Filament.—The relation of the distribution curves for short filaments to those for long filaments is shown, and it is pointed out that there is a family of reduced distribution curves from which any one desired curve may be obtained.

The Ribbon Filament.—Equations and conclusions developed for cylindrical or wire filaments apply equally well to filaments with rectangular and other cross-sections when the ratio of twice the cross-section to the perimeter of the filament is substituted for the radius of the cylindrical filament. For equivalent filaments (equal resistances and wattages at the same operating temperatures) operated at the same temperature, the percentage end-losses are the same.

REFERENCES.

[1] HYDE, CADY, and WORTHING, *Trans. Ill. Eng. Soc.* (U. S.) 6, p. 238, 1911; HYDE, *Ill. Eng.* (London) 4, p. 389, 1911.

[2] AMRINE, *Trans. Ill. Eng. Soc.* (U.S.) 8, p. 385, 1913.

[3] WORTHING, *Phys. Rev.*, 4, p. 524, 1914.

[4] WORTHING, *Phys. Rev.*, 4, see footnote, p. 538.

[5] WORTHING, *Phys. Rev.*, 5, p. 445, 1915.

[6] LANGMUIR, *Phys. Rev.*, 7, p. 151, 1916; *Gen. Elec. Rev.*, 19, p. 210, 1916; *Trans. Faraday Soc.*, 17, p. 621, 1922.

[7] STEAD, *Inst. Elec. Eng.*, 58, p. 107, 1920.

[8] WORTHING, *Phys. Rev.*, 10, p. 377, 1917.

[9] WORTHING and FORSYTHE, *Phys. Rev.*, 18, p. 144, 1921. (See also paper to be published soon.)

[10] HYDE, FORSYTHE and CADY, *Phys. Rev.*, 13, p. 45, 1919.

[11] WORTHING, *Astro. Jour.*, 36, p. 345, 1912.

[12] DAVISSON and GERMER, *Phys. Rev.*, 19, p. 438, 1922.

Preparation of Perchlorates by Heating Chlorates.—MATHERS and JONES, respectively of the Indiana State University and the Research Department of the Roessler and Hassler Chemical Company, St. Alban's, Vermont, have investigated the comparative yields of the electrolytic and direct heating processes for obtaining perchlorates. They failed to find any method by which the yield in the heating process can be increased over that heretofore obtained. Additions of different substances were made in hopes of establishing a catalytic effect, but none served the purpose, and most decreased the yield. The maximum yield was obtained by heating from 1 to 50 grams of potassium chlorate at from 480 to 560° C. for from 30 to 60 minutes. The yield was about 55 per cent. Sodium chlorate gave lower results, and several other chlorates were largely decomposed to chloride. The use of perchloric acid for electrolytic purposes makes its production important. H. L.

Lectures Before Local Sections of the American Chemical Society.—Arrangements have been made through the American Chemical Society for lectures to be delivered before the local sections by Professor E. C. Franklin of Leland Stanford University on dates during the latter part of March and early part of April. Several sections have already fixed dates. Applications for lectures should be made to E. M. Billings, Kodak Park, Rochester, New York. H. L.

The Luminescence of Incandescent Solids. E. L. NICHOLS and H. L. HOWES. (*Phys. Rev.*, April, 1922).—Any incandescent solid emits light because of its high temperature. Here we learn that there are solids that in a state of incandescense emit light not due to their temperature. The presence of luminescence is esablished whenever it can be shown that the body emits more intense light of any wavelength than is emitted at the same temperature by a black body, the best radiator by reason of temperature alone. At 665° C. CaO emits only .00432 as intense red light as a black body sends out. This fraction becomes three times as great at 735° C., twenty-six times as great at 837° and passes through two maxima before 1606° is reached, but at no temperature does it equal unity. There is thus no luminescence in respect to red. With blue it is quite a different story. The ratios which above were proper fractions are for blue light the following whole numbers for the four temperatures named—216, 52, 14, and .232. The result is so surprising that it merits setting forth in bold relief. Calcium oxide at a temperature at which it is barely luminous emits blue light 216 times as intense as that emitted by a black body at the same temperature. At the same temperature the corresponding ratio is for Al_2O_3, 400; SiO_2, 195; ZrO_2, 53; NbO, 2150. For NbO at 560° C. the ratio is 85,200, an astounding outcome. Luminescence in the red as well as in the blue was found in the cases of the oxides of praesodymium, neodymium, erbium, cerium, gallium, niobium, samarium, gadolinium, aluminium, zirconium, silicon and beryllium, and several points of maximum value are common.

The heating of the oxide under observation was done by the use of an oxy-hydrogen flame with a small content of oxygen. The use of this heating agent was determined by the fact "that the effect we were seeking is only indirectly related to temperature but is greatly stimulated and enhanced by the conditions existing in the oxy-hydrogen flame."

When an oxide was heated for the first time the intensity of the light emitted was greatest at first and diminished with time. For magnesium oxide the ratio was 65 at an instant .3 sec. after ignition. After several minutes it became less than one.

The authors connect the phenomenon they describe with changes in the physical state of the oxides, such as the electrical resistance. "It is as though during such rearrangements in the structure, the light-producing process which we term luminescence can go on."

G. F. S.

THE SAMPLING AND ANALYSIS OF AUTOMOBILE EXHAUST GAS.*

BY

A. C. FIELDNER AND G. W. JONES.

U. S. Bureau of Mines.

INTRODUCTION.

Analyses of samples of exhaust gas taken during road tests of 101 automobiles and trucks [1] under normal conditions showed an astonishing loss of gasoline due to incomplete combustion, and at least half of this loss could have been prevented by proper adjustment of their carburetors. A simple determination of the percentage of carbon dioxide in the exhaust gas affords a ready and scientific means of determining the completeness of combustion, and of adjusting the carburetor to give maximum efficiency. Part or complete gas analyses are valuable to the automotive engineer in solving problems in vaporization, manifold condensation, distribution to the cylinders, and combustion in the cylinders. The total volume of exhaust gases, the air-gasoline ratio, and the percentage of completeness of combustion may be calculated from the gas and gasoline analyses, and the quantity of gasoline used. It may be of some value, therefore, to the automotive and petroleum industries, to describe the methods of sampling and analyzing exhaust gases which were developed and used by the Bureau of Mines in connection with investigations pertaining to the ventilation of vehicular tunnels [2] and fuel economy in internal combustion engines.[3]

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* Communicated by the Director of the Bureau of Mines.

[1] Fieldner, A. C., Straub, A. A., and Jones, G. W., Bureau of Mine Reports of Investigations, Serial No. 2225, March, 1921.

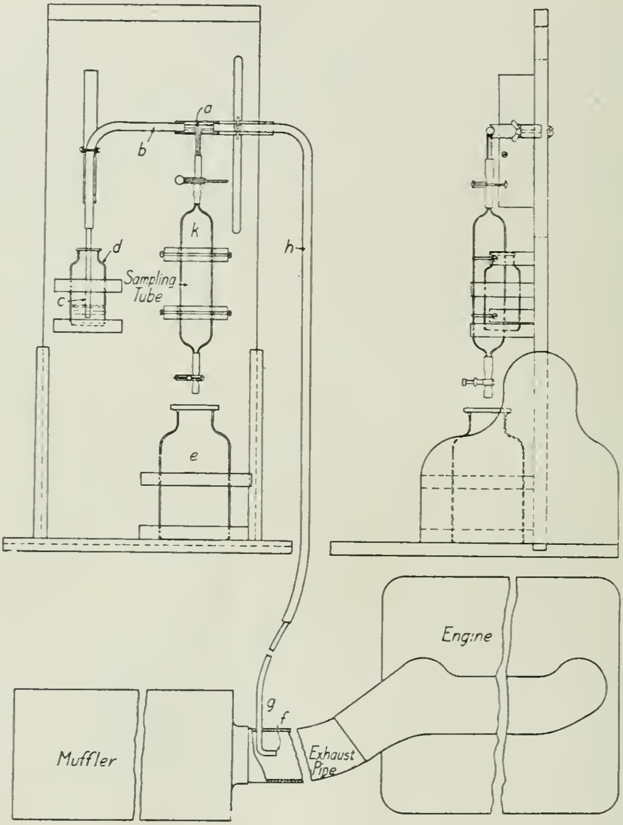
[2] Fieldner, A. C., Appendix No. 3—Tunnel Gases Investigations—Amount and Composition of Automobile Exhaust Gases; pages 91 to 140, Report of the New York State Bridge and Tunnel Commission 1921, Legislative Document No. 64 (1921).

[3] Fieldner, A. C., Straub, A. A., and Jones, G. W., "Gasoline Losses Due to Incomplete Combustion in Motor Vehicles," *Jour. Ind. Eng. Chem.*, vol. 13, 1921, pp. 51; *Jour. Soc. Automotive Engineers*, vol. 8, p. 295; Bureau of Mines Reports of Investigation, Serial No. 2225, March, 1921.

METHODS OF SAMPLING EXHAUST GASES IN ROAD TESTS.

A convenient apparatus for taking exhaust gas samples is shown in Fig. 1. The sampling tube *g*, of 1/4, 5/16, or 3/8-inch copper tubing, depending upon the size of car or truck, is introduced in the exhaust manifold between the engine and the muffler, with the opening *f* turned directly against the flow of gases. A gas-tight fit is obtained by using a clamp in two halves made to fit snugly around the exhaust pipe, and held in place by four bolts passing through both sections of the clamp. The copper tube is brazed into the upper half of the clamp, and is made gas-tight where it passes through the exhaust pipe by a layer of asbestos and graphite packing. The copper tube is extended

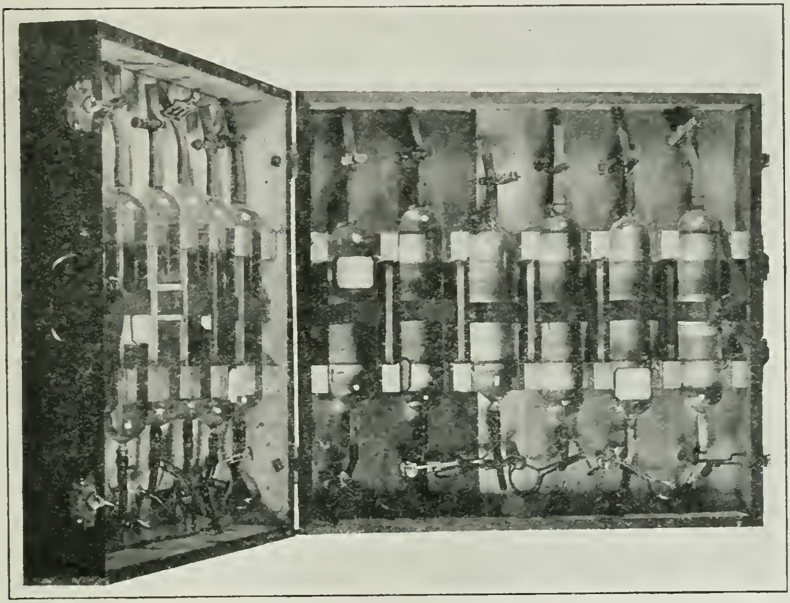
FIG. 1.



Attachment for taking samples of exhaust gas.

back along the exhaust pipe (to prevent freezing of moisture in cold weather), and up through the floor of the car where connection is made to a ¼-inch heavy-walled rubber tube *h*, which is connected to the glass tee *a*. The main stream of exhaust gases passes on through the rubber tube *b*, and is discharged into the atmosphere through the water-seal *c*, in the bottle *d*, thus preventing any air from being sucked back into the sample. A rapid stream of gas should flow out at the water-seal when the engine is running. The gas sample containers, or sampling tubes *k*, are of 250 c.c. capacity, and are made of glass tubing about 1½ inches in diameter, drawn out and sealed to capillary tubes to fit a 3/16-inch rubber tube at each end. The rubber connections are carefully wired gas-tight. Heavy-walled composition rubber tubing is best adapted for use with the screw-clamp which regulates the rate of discharge of the water from the lower end of the container, and 3/16-inch pure gum rubber tubing gives a gas-tight seal with a strong spring clamp at the upper end of the container.

FIG. 2.



Carrying cases for sampling tubes.

The sample containers are completely filled in the laboratory with water containing 5 per cent. sodium chloride, and are saturated with exhaust gases to reduce the solubility of carbon dioxide, and are transported in wooden carrying cases, as shown in Fig. 2. The water-filled container is attached to the tee *a* (Fig. 1) by slipping the pure gum tubing moistened with water over the lower branch of the tee, and is held in place on the board by two rubber bands as shown. The gas sample is then taken continuously over the whole period of a given test, by opening the upper pinch-clamp and the screw-clamp on the lower end of the container, and adjusting it to allow the container to become empty at the exact time for terminating the test. The water flows into the jar *e*, and this water is returned to the laboratory for refilling other sample containers. One observer should give his entire attention to taking the gas samples and regulating the flow of water from the gas-sample container by readjusting the screw-clamp at regular intervals, so that all the water is displaced by gas at the end of the test. No water should remain in contact with the gas other than which adheres to the walls and the few drops that remain in the capillary ends of the container.

ACCURACY OF SAMPLING METHODS.

The securing of a gas sample which represents the average composition of the entire quantity of exhaust gas produced during a given test with a fair degree of accuracy is of fundamental importance in determining the quantity of each constituent produced. Two methods of procedure may be considered, namely, (1) taking three or more intermittent or "grab" samples in each test and averaging the analyses; and (2) taking a single continuous sample of exhaust gas at a uniform rate during the entire period of each test.

GRAB OR INTERMITTENT METHOD OF SAMPLING.

In this method the sample container of glass or metal, fitted with stopcocks at each end, is attached to a short metal tube ¼ inch in diameter, which is inserted in the exhaust-gas manifold between the muffler and engine, as shown in Fig. 25, of Bureau of Mines Bulletin 74.[4] The exhaust gas is allowed to flow through the container for a sufficient length of time to ensure complete purging of the air. Both stopcocks are then closed, and the container is removed for analysis of the contents.

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[4] Hood, O. P., Kudlich, R. H., and Burrell, G. A., "Gasoline Mine Locomotives in Relation to Safety and Health," Bull. 74, Bureau of Mines, 1915, 84 pp.

Advantages of Grab Method.—(a) No confining liquid is necessary, and errors of solution of exhaust gases in this liquid are eliminated.

(b) It is simple and convenient to carry out during road tests.

Disadvantages of Grab Method.—(a) It represents only a small fraction of the test, therefore three or more samples would be required in each test to give a representative average analysis. Road tests of automobiles are subject to fluctuating power demands and constant changes of throttle position, so the analysis of each of these many samples would entail much more work than would be connected with taking a representative average sample which would include all variations during the entire test.

(b) There is danger of the exhaust gas not completely displacing the air in the containers.

CONTINUOUS METHOD OF SAMPLING.

A properly taken continuous, or rather proportional, sample should be of exactly the same composition as the entire exhaust gas given off during a test. While it cannot be taken in an exact proportion to the quantity of gas given off at each moment, it can be taken at a uniform rate throughout the test by regulating the flow of a fluid from the container; and if the test course and speed is fairly uniform, the sample should also be approximately proportional, at least more so than a small number of grab samples.

POSSIBILITY OF ERRORS.

Although mercury is the ideal fluid for use in continuous gas sampling because none of the gases dissolve in it, the large number of samples that may be taken each day while on the road makes the use of mercury practically out of the question. The use of water was therefore investigated with especial reference to the magnitude of possible errors resulting from solution of carbon dioxide, as this is the only constituent of exhaust gases that is materially soluble in water. In order to reduce the opportunity of solution, a narrow tubular gas sample container was used, so that only a comparatively small surface area of water was in contact with the gas. The solubility of carbon dioxide in water varies with the temperature; at ordinary room temperature, 1 c.c. of distilled water will absorb approximately 1.0 c.c. of carbon dioxide, if the gas above the liquid is 100 per cent. carbon dioxide. As the percentage of carbon dioxide decreases the amount absorbed diminishes; 14.6 per cent. carbon dioxide is the maximum possible quantity in exhaust gases with complete combustion of gasoline containing 85 per cent. carbon.

Error Due to Absorption of Carbon Dioxide.—The following series of tests were made in which air containing various known quantities of carbon dioxide was sampled simultaneously in two parallel sampling outfits similar to those used in the automobile tests. Mercury was used in one container and water in the other.

1. Carbon dioxide absorbed in tap water under sampling conditions, from a 15 per cent. CO_2-air mixture:

Experiment No.	Carbon dioxide, per cent. By mercury.	By water.	Difference.	Time to collect sample in minutes.
1	15.2	14.2	1.0	20
2	15.0	14.2	0.8	10
3	14.9	14.0	0.9	5

2. Carbon dioxide absorbed in water previously saturated with air containing 20 per cent. of CO_2, under sampling conditions, from a 19 to 20 per cent. CO_2-air mixture:

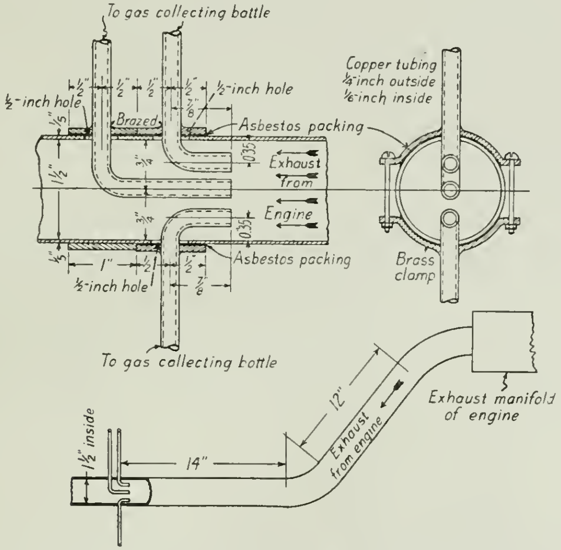
Experiment No.	Carbon dioxide, per cent.		Difference.	Time to collect sample in minutes.
	By mercury.	By water saturated with 20 per cent. CO_2 in air.		
1	19.5	19.1	0.4	20
2	18.6	18.4	0.2	20
3	19.5	19.1	0.4	10
4	18.6	18.6	0.0	10
5	18.6	18.6	0.0	5

3. Carbon dioxide absorbed or given off from the same water solution used in gas containers of previous experiment, under sampling conditions, from a 12 per cent. CO_2-air mixture:

Experiment No.	Carbon dioxide, per cent.		Difference.	Time to collect sample in minutes.
	By mercury.	By water from previous experiments.		
1	11.8	12.1	0.3	20
2	11.8	11.8	0.0	10
3	11.8	11.6	0.2	5

These experiments show a maximum error of 1 per cent. in the carbon dioxide content when using tap water over a sampling period of 5 to 20 minutes. Water saturated with a 20 per cent. CO_2-air mixture, and used in sampling air containing 20 per cent. CO_2, and subsequently in sampling air containing 12 per cent. of CO_2, showed differences or errors not exceeding 0.2 to 0.3 per cent. Therefore, it is safe to assume that the error due to absorption of CO_2 will never exceed 0.5 per cent. of the sample analyzed if the water is first saturated with air containing 10 to 12 per cent. of carbon dioxide, and then this same water is used repeatedly. In the Bureau of Mines road tests, 5 per cent. of sodium chloride was dissolved in the water to lower further the solubility of carbon dioxide, also to lower the freezing temperature of the water, as many of the tests were made in extremely cold weather.

FIG. 3.



Sketch of position of sample tube to check gas composition at various points,

Errors Due to Position of Sampling Tube in Exhaust Pipe.—In order to determine the composition of the exhaust gases at different points in the cross-section of the exhaust pipe, and to ascertain how closely a sample tube placed in the centre represented the average composition, a series of tests were conducted with sample tubes in different positions as follows:

Three sample tubes were fixed in a transverse plane of the exhaust pipe, respectively at ¼, ½, and ¾ of the inside diameter of the pipe. In conducting these tests, the motor was allowed to run sufficient time to become thoroughly warmed. Gas sample collecting tubes were then attached to each of the sampling tubes. (See Fig. 3.) The three samples were drawn at the same uniform rate for the period of the test. Tests were made on two different dates with the car standing, engine racing and engine idling. On each test and on each date, duplicate exhaust gas samples were taken for each condition of operation, during which time neither the position of the spark nor throttle was changed. The tests were each of four minutes' duration, and the percentage of CO_2 in the gas samples collected are shown by Table I, following:

TABLE I.

Results of Tests on Position of Sampling Tube in Exhaust Pipe Tests, Showing Variation of CO_2 Percentage in Samples Taken from Different Pionts.

		CO_2 in exhaust, per cent.				
Test No.	Test condition.	Top.	Centre.	Bottom.	Average CO_2 per cent.	Variation of average from centre sample, per cent.
1 - A	Standing, engine racing	9.8	9.7	8.3	9.3	—0.4
1 - B	Standing, engine racing	9.0	9.3	9.0	9.1	—0.2
2 - A	Standing, engine idling	6.7	6.8	6.5	6.7	—0.1
2 - B	Standing, engine idling	6.0	6.6	6.2	6.3	—0.3
3 - A	Standing, engine racing	9.6	9.4	9.4	9.5	+ 0.1
3 - B	Standing, engine racing	9.9	9.6	9.8	9.8	+ 0.2
4 - A	Standing, engine idling	6.5	6.3	5.8	6.2	—0.1
4 - B	Standing, engine idling	6.3	6.3	5.1	5.9	—0.4
	Average	8.0	8.0	7.5	—	0.2

The tests indicated as A and B are repeat tests made on the same day under the same conditions. The maximum variation of the percentage of CO_2 in the exhaust sample taken from the centre position when compared with the top, middle, and bottom was found to be 0.4 per cent., and the average of the average variation is 0.2 per cent. It will be noted that repeat tests under the same conditions may vary by 0.4 per cent., therefore the sampling of the exhaust from the centre is justified, and is within the experimental error of making duplicate tests under the same condition.

Further justification of placing the sampling tube in the centre of the exhaust pipe is shown by results obtained during tests made to check the quantity of exhaust gas liberated by an engine first as calculated from the gasoline used and the exhaust gas analysis, and secondly, by actually measuring the gases by running them into a 50-cubic foot tank from which water was run out as fast as the gases were introduced. During these tests, a continuous sample of the gas was taken from the centre of the exhaust pipe, and then after the gas in the tank was measured, a sample was taken from the top, middle, and bottom of the tank. The amount of CO_2 in these samples is shown in Table II. The maximum variation of the three tank samples, compared with the continuous sample taken from the centre of the exhaust pipe, show a remarkably close agreement, the maximum CO_2 per cent. variation being only .1 per cent.

TABLE II.

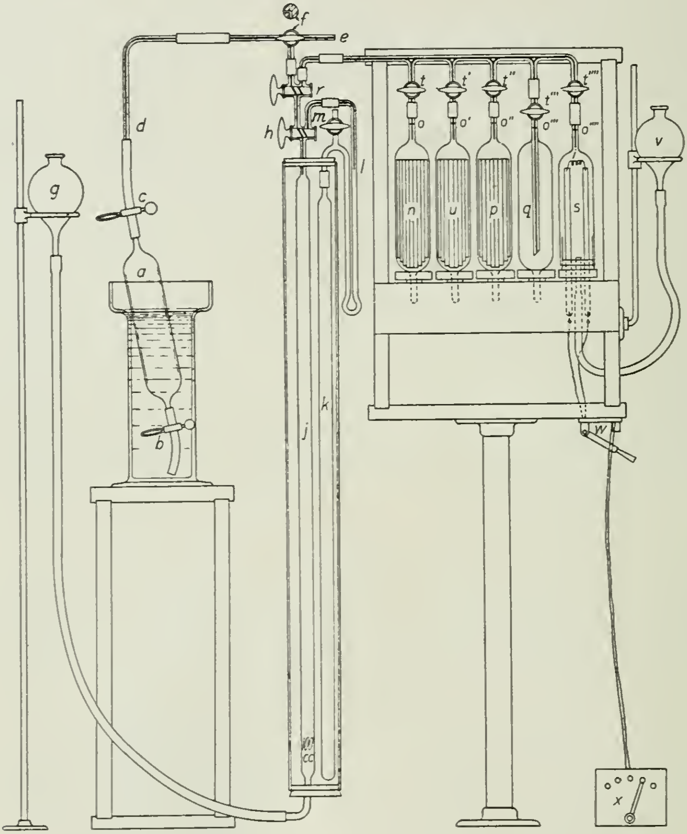
Results of Tests Showing Accuracy of Method of Sampling Exhaust Gas from Centre of Exhaust Pipe, as Compared with Sampling Total Exhaust Liberated. (Only the CO_2 percentages are given to show variation of composition of exhaust gas taken from centre of exhaust pipe and in tank.)

Test	CO_2 in exhaust gas in tank, per cent.			Average CO_2 per cent.	CO_2 in continuous sample from middle of exhaust pipe, per cent.	CO_2 variation per cent.
No.	Top.	Middle.	Bottom.			
1	7.6	7.7	7.8	7.7	7.7	0.0
2	5.6	5.9	5.8	5.8	5.7	0.1
3	5.7	6.1	6.0	5.9	6.0	0.1

COMPLETE ANALYSIS OF EXHAUST GAS.

Apparatus.—Complete analysis of exhaust gas includes the determination of CO_2, O_2, CO, H_2, CH_4, C_2H_4, and N_2 (by difference). The CH_4 determination is not strictly all methane, but is really the methane equivalent of the hydrocarbons in the gas. The special modified type of Orsat apparatus, shown in Fig. 4, is best adapted for speed and accuracy in analyzing exhaust gases. It consists essentially of a 100 c.c. water-jacketed burette *j*, compensating tube *k*, four absorption pipettes *n*, *u*, *p*, and *q*; and slow combustion pipette *s*. Mercury is used as the confining fluid in the burette and combustion pipette, and for displacing the sample in the container *a*.

FIG. 4.



Laboratory apparatus for complete analysis of automobile exhaust gases.

The burette is graduated in 1/10 c.c., every fifth mark extending half-way around the burette. The even cubic centimetres are etched on the burette, and the 100-c.c. mark is placed at the bottom. The tubes *n*, *u*, and *p* are simple absorption pipettes filled with the proper reagents and glass tubes to give better contact between the gas and absorbent; *n* contains potassium hydroxide solution for absorbing carbon dioxide, *u* contains fuming sulphuric acid for absorbing unsaturated hydrocarbons, and *p* contains potassium pyrogallate solution for absorbing oxygen. The tube *q* is a bubbling pipette, and contains acid cuprous chloride solution for absorbing carbon monoxide. Enough reagent is placed in each pipette so that when they are drawn to the marks o, o', o'', and o''', sufficient reagent remains in the rear branch of the pipette to form an adequate seal. Rubber bags should be attached to the rear branches of each pipette to prevent access of air to the reagents.

The combustible gases, consisting of methane (hydrocarbons), hydrogen, and carbon monoxide, not absorbed by the cuprous chloride, are burned by slow combustion in the pipette *s*, which contains a platinum coil *i* of No. 30 B. & S. gage wire 2¼ inches long. The ends of the coil are inserted in the tops of two glass tubes extending out through the rubber stopper in the bottom of the pipette. Stout loops of platinum wire are sealed into the bottom of these tubes. For 110-volt a. c. current, these loops are connected to the secondary of a 150-watt toy transformer having a variable voltage ranging from 1½ to 30 volts. A piece of No. 32 B. & S. gage nichrome wire 16 inches long is stretched between two binding posts mounted on the bottom board of the wood frame above the switch *w* (not shown in the figure). The binding post on one end of this wire and a sliding contact on it are connected into the circuit to permit close adjustment of the temperature of the platinum coil. The glass tubes in the combustion pipette are filled with mercury to complete the electrical circuit before inserting them in the pipette. After the pipette is mounted in place, mercury is poured into the bulb *v* until the level o'''' is reached.

Leveling bulbs *g* and *v* are supported by iron stands and adjustable ring supports as shown in the figure.

A good Orsat apparatus calls for the highest grade of workmanship in construction and assembling of the parts. The capillary train should be of 1½ to 2 mm. inside bore and of 7 mm. external diameter, so that tight connections may be maintained throughout. It should all be made of the same kind of glass, and must be well annealed. Above all, the stopcocks must have liberal bearing surfaces and must be accurately ground. The stopcocks should be lubricated with a special stopcock grease consisting of 50 parts by weight of pure gum rubber, 10 parts of vaseline, and 25 parts of beeswax.

Operating Procedure (Testing Tightness of Apparatus).—Draw into the burette about 50 c.c. of air, then turn cocks *h* and *r* to communicate with the train of pipettes. Raise the levelling bulb *g* so as to place the confined gas under a pressure of about eight inches of mercury. Any leaks in the stopcocks or rubber connections are shown by the mercury slowly rising in the burette. This procedure, however, does not indicate any leaks in the rubber connections below stopcocks t, t', t'', etc. Any leaks at these connections are shown by the solutions falling from the marks o, o', o'', and o''', after standing for a time.

Measuring the Sample.—Before beginning a series of analyses, see that the compensator tube *k* and the burette contain enough water to ensure saturated gases, and that the compensator U-tube *l* is filled with mercury to mark *l*. Sweep the capillary train free from oxygen by drawing a sample of air into the burette and passing it into the "pyro" pipette *p* until all the oxygen is removed. Then pass this nitrogen through all the other pipettes to remove oxygen. In succeeding determinations this preliminary removal of oxygen is unnecessary, as nitrogen only remains in the apparatus after an analysis. Adjust the gas in the compensator tube to atmospheric pressure by momentarily removing the three-way cock *h* and compensator cock *m*. Adjust all the reagents in the absorption pipettes and the mercury in the combustion pipette to the marks *o* on the capillaries.

Turn stopcocks *h*, *r*, and *f* to communicate with the outside air at *e*, slowly raising levelling bulb *g* until the mercury reaches *f*. Connect the exhaust gas sample tube with *d*, and dip the lower end into the mercury container. Squeeze out all air bubbles from the rubber connection, then open the clamp *b*; turn stopcock *f* to communicate with the sample, lower levelling bulb *g* slightly, and open clamp *c* at top of sample tube, allowing about 30 c.c. of gas to enter the burette. Reject this sample through cock *f* and the free end *e*, as it is contaminated with air from the connections. When the mercury reaches *f*, turn the cock to communicate with the sample, and draw about 50 c.c. of sample into the burette as previously directed. Close pinch-clamp *c*, turn *r* through 180 degrees connecting to the absorption train, and then turn *f* to the air.

Now turn *h* through 180 degrees, thus connecting the burette and compensator, and raise or lower bulb *g* until the mercury in the compensator U-tube reaches the mark *l*. Read and record the volume of sample taken to the nearest 0.05 c.c.

Carbon Dioxide.—Turn *h* through 180 degrees, and raise levelling bulb *g* slightly to put the sample under pressure, thus avoiding any possibility of pulling the caustic solution into the cock *t*; then turn cock *t* to admit the sample from the burette to the caustic pipette, continue raising *g* slowly until the mercury reaches *h*; lower the levelling bulb slowly, drawing the gas back into the burette until the caustic solution covers the glass tubes in the pipette; again pass into the caustic pipette, and return it to the burette, repeating this operation until all of the CO_2 is absorbed. Finally, bring the level of the reagent to the mark *o* very carefully to avoid getting any solution into the stopcock *t*; close stopcocks *t*, turn *h* to communicate with the compensator, and adjust the mercury level in the compensator manometer to the mark *l*. Read and record the volume of gas. Repeat the above operations until no further contraction in volume takes place. If more than 10 passes are required to get complete absorption, the caustic solution should be replaced with a fresh one. The final burette reading subtracted from the original volume is the contraction due to the absorption of carbon dioxide.

$$\text{Percentage of } CO_2 = \frac{\text{Contraction} \times 100}{\text{c.c. of sample taken.}}$$

Unsaturated Hydrocarbons.—Pass the gas six times into the fuming sulphuric acid pipette, then remove the SO_3 vapors by passing the gas into the caustic pipette *n*, and return it to the burette for reading the contraction as prescribed under the determination of carbon dioxide.

$$\text{Percentage of unsaturated hydrocarbons} = \frac{\text{Contraction} \times 100}{\text{c.c. of sample taken.}}$$

Oxygen.—Pass the gas into the pyrogallate pipette 12 times, read and record volume. If the volume does not remain constant after 12 passes, the solution should be renewed.

$$\text{Percentage of oxygen} = \frac{\text{Contraction} \times 100}{\text{c.c. of sample taken.}}$$

Carbon Monoxide, Hydrogen, and Methane.—Pass the gas slowly through the cuprous chloride pipette *g* several times to remove the bulk of the carbon monoxide, and then into KOH pipette to remove acid vapors. Return the sample to the burette; adjust the compensator level to the mark, and read the volume. The contraction in cubic centimetres is the volume of carbon monoxide absorbed by cuprous chloride, and is to be added to the remainder of the carbon monoxide determined later by combustion, to get the total volume of carbon monoxide in the sample.

Turn cock *h* through 180 degrees, and lower levelling bulb *g*, placing the sample under slightly reduced pressure. Turn cock *r* to communicate with the atmosphere through *f*, and draw sufficient air (approximately 25 c.c. for exhaust gases) into the burette to burn all the combustibles in the sample. Adjust the compensator and read the total volume. Turn cocks *r* and *h* 180 degrees, open cock t'''', and pass the mixture into the combustion pipette *s* by lowering bulb *v* and raising *g*. Close the switch *w*, and raise the temperature of the platinum wire to a bright yellow. Pass the gas back and forth over the hot platinum wire by raising and lowering the levelling bulb *g*, at the same time moving the levelling bulb *v* to keep the surface of the mercury in this bulb on the same level as the mercury in the combustion pipette; keep the combustion pipette cool by playing a stream of compressed air on the upper part of the pipette. After the combustion is complete, cut off the current and allow the pipette to cool, and return the gas to the burette by lowering levelling bulb *g* and raising *v*, bringing the mercury level to the mark o'''' and closing the cock t''''. Read and record the volume. The difference in volumes is the contraction due to combustion.

Pass the gas into the caustic pipette to remove and determine the carbon dioxide formed by combustion. Read and record the difference in volume as carbon dioxide from combustion. Finally pass the gas into the pyrogallate pipette repeatedly to absorb and determine the residual oxygen.

From the CO absorbed by cuprous chloride, the contraction on combustion, the CO_2 from combustion, and the residual oxygen, the total carbon monoxide, hydrogen, and methane are computed as follows:

$$\text{Percentage of hydrogen} = \frac{(\text{Contraction} - \text{oxygen consumed})\ 100}{\text{c.c. of sample taken}}$$

$$\text{Percentage of methane}^{5} = \frac{(\tfrac{2}{3}\,\text{contraction} - \tfrac{1}{3}\,CO_2 - \text{c.c.H})\ 100}{\text{c.c. of sample taken}}$$

$$\text{Percentage of carbon monoxide} = \frac{(\text{CO by } CuCl_2 + CO_2 \text{ formed} - \text{c.c. } CH_4)\ 100}{\text{c.c. of sample taken}}$$

The following data sheet of an exhaust gas analysis illustrates the above calculations:

Data Sheet of an Exhaust Gas Analysis.

Car, Hudson		Laboratory No. 11869	
Apparatus, Orsat No. 12.		Bottle No. 11 c.c.	

		Burette reading.	Difference.	Per cent.
A	Volume of sample taken	49.90		
B	Carbon dioxide	44.95	4.95	9.9
C	Unsaturated hydrocarbons	—	—	—
D	Oxygen	43.70	1.25	2.5
E	CO by Cu_2Cl_2	41.95	1.75	—
F	Total volume	66.65	—	—
G	Air added	24.70	—	—
H	Equivalent oxygen = $G \times 0.209$	—	5.15	—
I	Volume after burning	64.60	2.05	—
J	Volume after CO_2 absorption	64.20	0.40	—
K	Residual oxygen	60.15	4.05	—
L	Oxygen consumed = H − K	—	1.10	—
M	Hydrogen = I − L	—	0.95	1.9
N	Methane = [(21 − J) ÷ (3 − M)]	—	0.30	0.6
O	CO = J − N	—	0.10	—
P	Total CO = E + O	—	1.85	3.7
S	Nitrogen (By difference) Determined by difference	—	—	81.4

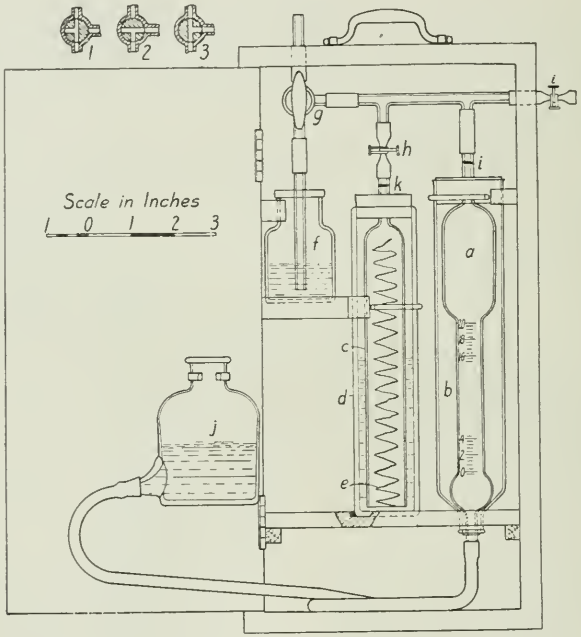
---

[5] In exhaust gas analyses, the term "methane" really means the volume of methane equivalent to the total hydrocarbons, as other hydrocarbons as gasoline vapor may also be present.

PORTABLE ORSAT APPARATUS FOR DETERMINING CARBON DIOXIDE ONLY.

A simple portable apparatus for determining carbon dioxide only is sufficient for adjusting carburetors and determining the completeness of combustion. Fig. 5 illustrates a compact form of the well-known portable Orsat apparatus modified especially for carbon dioxide determinations on road tests. The entire apparatus weighs five pounds, and the outside divisions are 4½ by 7 by 14 inches.

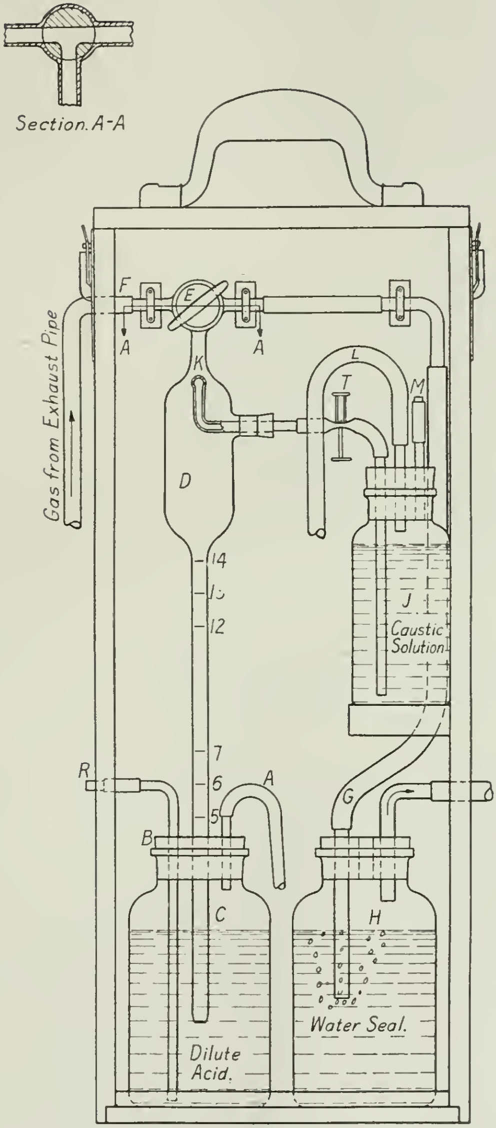
Fig. 5.



Portable Orsat apparatus for analysis of CO_2 in exhaust gas.

The water-jacketed burette *a* has a capacity of 100 c.c., and is graduated on the narrow point to read directly in percentage. Slightly acidulated water is used for the levelling fluid in the bottle *j*. The pipette *d* contains sodium hydroxide solution, containing 20 grams of NaOH in 100 c.c. of water for absorbing the carbon dioxide. The wavy line *e* represents a piece of sheet iron to expose a large surface of hydroxide solution to the gas. At *g* is a three-way glass cock, and *f* is a water-seal through which a rapid stream of exhaust gas is allowed to bubble while taking

FIG. 6.

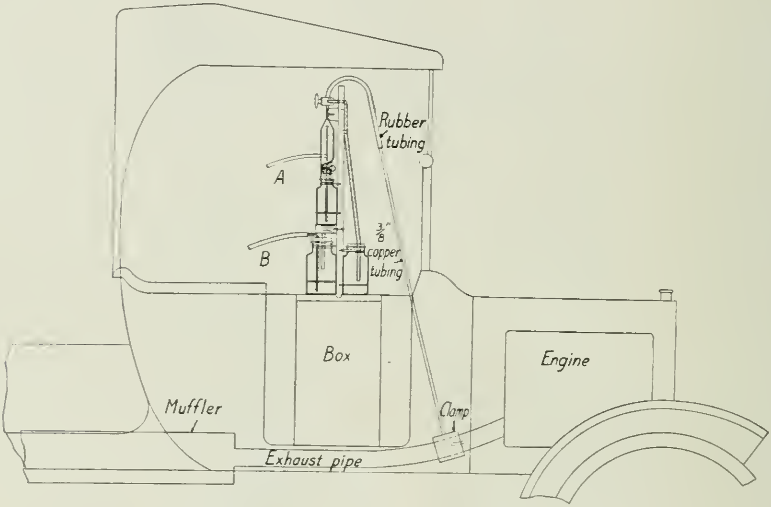


Details of portable CO_2 indicator.

the sample. The glass tube protruding out of the top of the box is connected with a heavy-walled rubber tube and a copper pipe to the exhaust pipe as shown in Fig. 7.

Procedure in Making a Carbon Dioxide Determination.—Turn *g* to position 1, and allow the exhaust from the engine to bubble through the water-seal *f* in a rapid stream. Raise levelling bottle *j;* open pinch-clamp *i,* and allow water-level in the burette to reach the mark *l* at the top of the burette; close *i,* lower *j,* and slowly open pinch-clamp *h,* raising the caustic solution to the mark at the top of the caustic pipette. Close *h,* open *i,* and again bring the water-level in the burette to the mark *l* by raising *j;* then close *i.* The apparatus is now ready for taking a gas sample. With one hand raise the levelling bottle *j* to the level of mark *l,* and with the other hand turn *g* to position 3, and slowly lower *j,* thus drawing a small part of the gas stream into the burette. Draw slightly more than 100 c.c. of gas into the burette, then turn *g* to position 1. Raise *j* until the water-level in the burette reaches the zero mark at the bottom; close the rubber tube connecting the levelling bottle and burette by pinching the tube tight with the fingers, and open *i* momentarily to allow the sample in the burette to come to atmospheric pressure.

FIG. 7.



Method of connecting indicator to the exhaust for making analyses on the road.

Raise *j*, and open *h* slowly, forcing the gas into the caustic pipette. Pass the gas back and forth from the burette to the pipette until all the carbon dioxide is absorbed; six passes are usually sufficient. Lower *j* until the caustic potash solution reaches the mark *k*, close *h*, and after allowing the burette to drain one minute, bring the water in the burette and levelling bulb to the same level, and read the burette. This reading is the percentage of carbon dioxide in the sample. The caustic solution must be renewed when the reading does not remain constant on repeating the above operations.

CARBON DIOXIDE INDICATOR FOR AUTOMOBILE EXHAUST GASES.

The apparatus shown in Fig. 6 was especially designed by one of the writers (G. W. Jones) for the quick determination of carbon dioxide in automobile exhaust gases in road tests. This carbon dioxide indicator is of simple leak-proof construction, easy to operate by the layman, and yet accurate to within the required limits for efficiency tests and carburetor adjustment.

The essential feature of this indicator is the burette *D*, in which the carbon dioxide is absorbed from a measured sample of gas by spraying caustic soda solution from the jet *K* against the inside walls of the bulb *D*, thus causing the liquid in bottle *C* to rise in the slender graduated portion of the burette in proportion to the percentage of carbon dioxide absorbed from the sample.

A rugged three-way stopcock *E* with 6 mm. bore is sealed to the top of the burette.

The caustic jet *K* consists of a series of fine holes evenly spaced on the circumference of the end of the tube *K* at an angle of 45 degrees with the horizontal. From the bulb of the burette extends a slender tube of uniform bore graduated directly in percentages of carbon dioxide.

The lower end of the burette extends into the bottle *C* through the rubber stopper *B*. The bottle *C* is filled to the mark *Z* with a 5 per cent. solution of sulphuric acid by removing the glass plug *R* and inserting a piece of glass tubing, the other end of which dips into the reserve supply of the acid solution. The acid is then drawn into bottle *C* by applying suction to the rubber tube *A*. The glass tubing is then removed, and the glass plug is replaced.

The height of solution may vary one-half inch above and below the mark *Z* without effecting the accuracy of the results, but sufficient solution must remain at all times in the bottle to seal the lower end of the burette when filled with liquid ready for taking a sample.

Bottle *J* is filled with a 10 per cent. solution of caustic soda by removing glass plug *M,* and inserting a small funnel in its place. When bottle *J* is filled, the funnel is removed, and the glass plug *M* is replaced. Enough water is poured into bottle *H* to form a water-seal with the rubber tube extending into the bottle from *G.* After the caustic soda solution is blown to the tip of jet *K,* by blowing on rubber tube *L,* and opening pinch-clamp *P,* the indicator is ready for use.

Procedure in Making a CO_2 *Determination.*—To make an analysis, cock *E* is turned to the position as shown in section *A-A*, and by blowing in rubber tube *A*, liquid is forced into the burette, and when it reaches cock *E,* the same is turned 180 degrees, thus the burette is completely filled with the acid solution.

The copper tubing leading from the exhaust manifold is connected to the indicator at *F* by heavy-walled rubber tubing. The pressure is sufficient to force a stream of gas from the muffler through cock *E,* and out through the water-seal *H.* When the line has been purged with gas, a sample is taken into the indicator by turning cock *E* 90 degrees to the left, thus allowing the liquid in the burette to fall and pull in a sample of gas, the pressure on the line forcing the gas out through the bottom of the burette into bottle *C.* Cock *E* is then turned 90 degrees to the right, and the gas in the burette is allowed to stand 30 seconds to permit it to come to the surrounding temperature, also to allow the burette to drain. Allowing the gas to stand and cool draws some liquid from *C* into the bottom of the burette, owing to contraction of the gas on cooling. At the end of 30 seconds, cock *E* is turned to the left, and enough gas is allowed to enter the burette to bring the gas volume to the bottom; *E* is then turned 90 degrees to the right. There is now a definite measured volume of gas in the burette at the same temperature as the indicator. Caustic soda is forced into the burette from the jet *K* by blowing on *L,* and at the same time opening pinch-clamp *P.* Six or more separate small charges of the caustic solution are forced into the burette in succession, allowing sufficient time for this solution to drain

TABLE III.

Laboratory Check between Portable and Orsat Apparatus.

Sample No.	CO_2 by indicator, per cent.	Average.	CO_2 by Orsat, per cent.
1	11.8		
	12.4		
	12.3		
	12.6		
	12.6	12.4	12.4
			Average error, % = 0.0
			Maximum error, % = 0.6
2	10.8		
	11.7		
	11.6		
	10.8		
	11.6		
	11.7	11.4	11.0
			Average error, % = 0.4
			Maximum error, % = 0.6
3	8.3		
	8.5		
	8.7		
	8.7		
	8.8	8.6	8.5
			Average error, % = 0.1
			Maximum error, % = 0.3
4	7.4		
	7.3		
	7.5	7.4	7.4
			Average error, % = 0.0
			Maximum error, % = 0.1

down the burette before the next charge is introduced. (An interval of ten seconds between each charge has been found sufficient.) If more time is allowed, the CO_2 is removed before the sixth charge is introduced, but the same result is obtained. The caustic soda solution sprayed into the burette quickly removes the CO_2, and the solution in *C* rises into the stem of the burette to a height depending upon the amount of CO_2 present. The highest point reached by the solution after the sixth charge has been introduced is the correct reading.

The indicator is made ready for another analysis by again blowing into tube *A*, and filling the burette as previously directed. When forced into the burette, the dilute sulphuric acid in *C* neutralizes the caustic soda solution each time, so there is no absorption of CO_2 while the sample is being taken and brought to the surrounding temperature.

A small quantity of solution is blown each time over into bottle *H* when the burette is filled, so that the liquid height in *C* is kept approximately at the level *Z*.

A few drops of phenolphthalein solution is added to the caustic soda solution, which turns pink the solution in *C* when it becomes exhausted.

The bottle *J* holds a sufficient caustic solution to make from twenty-five to thirty-five determinations, depending on how economically the solution is used.

Table IV.

Operation Check between Portable and Orsat Apparatus.

Sample.	Grade.	CO_2 by indicator, per cent.	CO_2 by Orsat, per cent.
1–A	Level	7.5	7.1
2–A	Level	10.0	9.1
3–A	Level	8.5	8.4
1–B	Level	12.5	13.1
2–B	Level	11.5	11.4
3–B	Level	11.0	10.9
1–C	3 per cent.	13.5	13.6
2–C	3 per cent.	13.8	13.3
3–C	3 per cent.	13.8	13.2
Average	——	11.3	11.1
Average error, per cent.			0.2
Maximum error, per cent.			0.9

It is important when the first charge of caustic soda solution is blown into the burette that only enough pressure is applied to barely cause the caustic solution to run down the sides of the jet, otherwise a small bubble of gas will be blown out of the bottom of the burette, and this in turn will give too large a percentage indication for carbon dioxide.

Accuracy of Indicator.—The accuracy of the indicator when operated under laboratory conditions is shown by the following results. (CO_2 and air mixture were prepared of varying concentrations and determinations made with the indicator. The CO_2 content was then checked by analyses on an Orsat gas apparatus.)

Table IV shows the accuracy that may be expected while adjusting carburetors on the road: (An automobile was operated at approximately 15 miles per hour on both level and 3 per cent. grades. One sample of the gas was taken into the indicator and analyzed directly for CO_2. Another was taken at the same time for laboratory analysis by the Orsat method.)

From Table IV it is seen that the average error during tests on the road is 0.2 per cent. when several samples are taken, and that individual samples may be in error as much as 1.0 per cent. In general, the individual determinations of the indicator may be regarded as accurate within 0.5 per cent. in most instances on road tests, and more accurate than this when, as should be done, a number of determinations are made and an average taken.

To determine how much the exhaust gas may vary on road tests under constant conditions, an automobile was run over a one-mile curve and up a 3 per cent. grade at 15 miles per hour. Arrangements were made so that three grab samples of the exhaust gas could be taken, also one continuous sample over the entire test period. Three grab samples were taken during each test and the following results were obtained:

	CO_2, per cent.						
Test No.	No. 1	Grab sample No. 2	No. 3	Average of grab samples, per cent.	Continuous samples, per cent.	Average variation, per cent.	Maximum variation, per cent.
1	9.9	9.0	9.4	9.4	9.3	0.1	0.6
2	8.8	9.7	9.1	9.2	9.0	0.2	0.7
3	9.4	9.4	8.5	9.1	9.1	0.0	0.6

All three of the above tests were made under the same conditions, and without changes in carburetor adjustments. It will be seen that the continuous samples vary for the three tests by 0.3 per cent., and therefore it is impracticable to use an apparatus more accurate than 0.3 per cent., as duplicate tests may give percentages of CO_2 which may vary by the above amount. This applies for continuous samples taken over an estimated time period. In the case of grab sampling, the variation of the exhaust gas is much greater, as shown. In one case the maximum variation equalled 0.7 per cent.

METHOD OF SAMPLING EXHAUST GAS FOR CO_2 DETERMINATIONS.

The procedure to follow in adjusting a carburetor by gas analysis depends upon the type of carburetor, and conditions under which the automobile or truck is usually operated. In every case, the final adjustment should be under actual operating conditions at speeds comparable to that at which the motor vehicle is operated. An exhaust sampling pipe should be fitted as previously described.

The exhaust gas coming from the engine under a slight pressure forces some of the gas out through the copper tube. This copper tube connects with the CO_2 indicator or portable Orsat—as the case may be—by a heavy-walled rubber tube. By putting the exhaust sampling tube in the position shown in Fig. 7, the floor boards in the front seat can be removed and the copper tube brought directly upward to the testing apparatus. A box of about 12-inch cross-section and 18 inches high is convenient for supporting the apparatus while making the tests. If the road over which the motor vehicle is operated is very rough, a 2 or 3-inch pad of cotton waste should be placed between the apparatus and the box to take up the vibration.

The motor vehicle to be tested should be driven two or three miles to get it thoroughly warmed up, then run at a speed at which it is usually operated, and several samples of the exhaust gas should be analyzed and recorded, after which it can be tested at other speeds in a similar manner. Should the percentage of CO_2 be low (especially below 10 per cent.), the carburetor adjustment should be made leaner and the tests repeated. The procedure is continued until the percentage of CO_2 is as high as possible, and still give flexible operation.

A definite value for the percentage of CO_2 that should be in the exhaust gas can not be given to apply to all makes of cars, and especially carburetors. Weather conditions also affect the adjustments. For example, the carburetor may be adjusted to give 13 per cent. CO_2 on a warm summer day, and left at this adjustment; a sudden change to colder weather may increase the viscosity of the gasoline so as to cause the mixture to be too lean for flexible operation.

In general, 12 per cent. of CO_2 or more in the exhaust is not too high a figure for smooth operation and economy of gasoline. When it is seen that most automobiles and trucks operate under conditions where the exhaust gas contains 9.5 per cent. of CO_2 or less, the adjustment of carburetors by exhaust gas analysis becomes very important.

INTERPRETATION OF EXHAUST GAS ANALYSIS.

Automobile exhaust gas consists of carbon dioxide, oxygen, carbon monoxide, hydrogen, methane, gasoline vapor, nitrogen, and traces of unsaturated hydrocarbons.

Carbon Dioxide.—This gas is formed by complete combustion of carbonaceous material. The amount of carbon dioxide in exhaust gas depends upon a number of factors, chief of which are the ratio of air to gasoline vapor (carburetor adjustment), thoroughness of mixing vapor and air, completeness of vaporization, and temperature and degree of compression in the cylinders. Under ideal conditions with the theoretical amount of air for complete combustion of the gasoline, the only products of the reaction or combustion should be carbon dioxide, water vapor, and nitrogen. The nitrogen comes from the air used for combustion. If an excess of air be present, the combustion products are carbon dioxide, water vapor, oxygen, and nitrogen. However, under practical operating conditions there is usually a small percentage of oxygen passing through into the exhaust gases, even when a deficiency of air is mixed with the gasoline vapors. The maximum possible percentage of carbon dioxide is formed in the exhaust gas when the theoretical amount of air is present, and there is perfect combustion of the hydrogen and carbon of the gasoline. This value varies slightly with the percentages by weight of carbon and hydrogen in the gasoline. Assuming a gasoline of 84 per cent. carbon and 16 per cent. hydrogen, then

	CO_2 lb.	H_2O lb.	N_2 lb.
0.84 lb. of carbon produces	3.08	—	7.43
0.16 lb. of hydrogen produces	—	1.44	4.25
Total of	3.08	1.44	11.68

The water condenses out and is not indicated in the exhaust gas analysis. Changing from a weight to a volumetric basis, by dividing by the molecular weights, we have

$$\frac{11.68}{28} = 0.417$$

$$\frac{3.08}{44} = 0.070$$

$$\text{Total} = 0.487$$

$$\frac{0.070}{0.487} \times 100 = 14.4 \text{ per cent. carbon dioxide by volume.}$$

$$\frac{0.417}{0.487} \times 100 = 85.6 \text{ per cent. nitrogen by volume.}$$

The maximum carbon dioxide content that can be obtained in the exhaust gases when the above gasoline is used is 14.4 per cent. When the exhaust gas indicates this value for carbon dioxide, the combustion is complete. Lower values are due either to incomplete combustion or excess air.

Oxygen.—This may be due to excess air (lean mixture), large excess of gasoline vapor (very rich mixture), incomplete vaporization, or poor mixing of the gasoline vapor and air in the engine. If the gasoline is not completely vaporized and is partly carried into the cylinder in the form of a mist consisting of small globules of liquid gasoline, the combustion is incomplete, especially at low speeds and before the engine gets warmed up. The oxygen cannot attack the gasoline in the interior of these particles in the short time interval of the explosion in the cylinder. This condition gives rise to free oxygen in the exhaust gases, together with high percentages of incomplete combustion products such as carbon monoxide, hydrogen and methane.

Carbon Monoxide.—This is the poisonous constituent of exhaust gases, and is formed by incomplete combustion of carbon. Unless an excess of air is present, and the gases are properly vaporized and mixed, carbon monoxide is produced in varying large quantities. Carburetor adjustment for feeding a rich mixture is the most general cause for the large quantities of carbon monoxide formed in the exhaust of most machines. The mixture may be so rich that the ignition takes place only in the neighborhood of the spark, and does not propagate itself throughout the whole charge. This condition produces large quantities of carbon monoxide and other unburned gases, such as hydrogen and methane, together with oxygen and gasoline vapor. Experiments made by Burrell[6] showed that when a mixture of 5 per cent. gasoline-vapor in air was exploded, 9 per cent. of unconsumed oxygen remained in the residual gases, and the flame travelled so slowly that it could be followed by the eye. When 4.1 per cent. gasoline-air mixtures were exploded, 3.4 per cent. of oxygen was found. This substantiates the fact that when rich mixtures are used in gasoline engines there may be large quantities of oxygen present in the exhaust gases accompanied by products of incomplete combustion.

The presence of carbon monoxide in automobile exhaust gases is not only objectionable on account of its poisonous nature, but it means a material loss in mileage per gallon of gasoline used. The average analysis of exhaust gas from the 101 cars and trucks tested by the Bureau of Mines showed about 6.5 per cent. carbon monoxide. This means that 30 per cent. of the heat in the gasoline was lost. With proper combustion in the engine, and correct carburetor adjustment, at least 20 per cent. greater mileage should have been secured per gallon of gasoline used. One of the cars was exhausting 13.2 per cent. of carbon monoxide, which corresponds to a loss of 50 per cent. of the gasoline used—an enormous and unnecessary waste of gasoline.

Hydrogen and Methane.—The hydrogen and methane in exhaust gases are the result of the decomposition of the gasoline in the absence of oxygen, and perhaps in a lesser degree to reactions in which water-vapor takes part. In a general way, the hydrogen increases proportionally with the carbon monoxide; and at adjustments at maximum power equals approximately 40 per cent. of the CO content. The percentage of methane is very low when the engine is running under the best conditions.

Gasoline Vapor.—The gasoline vapor in exhaust gases is due to poor ignition, poor mixing, and incomplete vaporization of the gasoline and air; also to rich mixtures, or incomplete flame propagation. One or several of these above conditions may cause small portions of the gasoline to pass through the engine without reacting with the oxygen present in the air.

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[6] Hood, O. P., Kudlich, R.H., and Burrell, G. A., "Gasoline Mine Locomotives in Relation to Safety and Health," Bull. 74, Bureau of Mines, 1915, pp. 69–71.

In the gas analyses, the gasoline vapor and all other hydrocarbons appear as methane. The analysis gives the equivalent methane value for all the hydrocarbons in the exhaust gas, and the result is correct as regards carbon content for computing the total volume of exhaust gases from the gasoline consumption and the carbon content of the gasoline. The determination of gasoline vapor as methane causes the hydrogen value in the analysis to be somewhat less than its true value. This error in the hydrogen value has no effect on calculation of the true volume of carbon monoxide, carbon dioxide, and methane equivalent of hydrocarbons produced in the tests.

Finally, it must be recognized that absolutely all the gasoline fed into the engine does not appear in the exhaust gas analysis. In cylinders with poorly fitting piston rings, and in very cold weather, some gasoline escapes into the crank-case, also traces of carbon remain behind on the cylinder walls. To partly compensate for this loss, some constituents of the exhaust gas undoubtedly came from the burning of lubricating oil in the cylinders.

Unsaturated Hydrocarbons.—These appear in exhaust gases at times, especially when the carburetor has a very rich adjustment. The exhaust gases in the road tests cited above were tested from time to time for unsaturated hydrocarbons. The amount present usually was not more than 0.1 per cent., the experimental error of analysis. In exceptional cases, where a very rich mixture was used, and the car was in poor adjustment, the percentage of unsaturated hydrocarbon was as high as 1 per cent. In order to keep the exhaust gas calculations correct, the unsaturated hydrocarbon value was doubled and reported as methane.

COMPUTATION OF VOLUME OF EXHAUST GASES.

Volume of Exhaust Gases.—The total volume of exhaust gases produced per gallon of gasoline consumed may be computed from the analysis of the exhaust gases and the weight and analysis of the gasoline. This computation is based on the assumption that all the carbon in the gasoline appears in the exhaust gases. As a matter of fact, there is a small error due to solid particles of carbon in the exhaust and on the motor surfaces, and leakage of gasoline into the crank-case. This error may be partly compensated, or exceeded in some cases, by lubricating oil burning in the cylinders. The total error is negligible, as shown by tests made with engine idling, in which the exhaust gases were collected and measured in a 50 cubic foot calibrated gas tank. The measured volumes checked to within 1 per cent. of the volumes computed from the analysis in the usual manner, when the average of four tests were taken and the maximum variation was 6 per cent.

COMPUTATION OF VOLUME OF EXHAUST GASES.

From the gasoline analysis:

a = sp. gr. of the gasoline at 60° F.
b = per cent. carbon in the gasoline by weight.
8.33 = weight of one gallon water, in pounds, at 60° F.
(1) $8.33ab$ = pounds of carbon in one gallon of the gasoline.

From the gas analysis:

c = per cent. CO_2 in the exhaust gas by volume.
d = per cent. CO in exhaust gas by volume.
e = per cent. CH_4 in exhaust gas by volume.
0.1158 = weight in lb. of 1 cu. ft. CO_2, 65° F. and 29.92 in. Hg.
0.0732 = weight in lb. of 1 cu. ft. CO, 65° F. and 29.92 in. Hg.
0.0420 = weight in lb. of 1 cu. ft. CH_4, 65° F. and 29.92 in. Hg.
$0.1158 \times 3/11$[7] $= 0.0316$ = lb. carbon in 1 cu. ft. CO_2 at 65° F. and 29.92 in. Hg.
$0.0732 \times 3/7$[7] $= 0.0314$ = lb. carbon in 1 cu. ft. CO at 65° F. and 29.92 in. Hg.
$0.0420 \times 3/4$[7] $= 0.0315$ = lb. carbon in 1 cu. ft. CH_4 at 65° F. and 29.92 in. Hg.
$0.0316c + 0.0314d + 0.0315e$ = total pounds of carbon in 1 cubic foot of exhaust gas. This expression may be simplified by using the mean value 0.0315 as follows:

(2) $0.0315\,(c + d + e)$ = total pounds of carbon in 1 cubic foot of exhaust gas.

Dividing by (1) and (2)

$$\frac{8.33\,ab}{0.0315\,(c+d+e)} = \frac{264.4\,ab}{c+d+e} = \frac{\text{cu. ft. exhaust gas at 65° F.}}{\text{29.92 in. of Hg. per gallon of gasoline.}}$$

The expression 264.4ab is constant for each gasoline, and represents the total cubic feet of carbon-containing gases (CO, CO_2, and CH_4) that is produced by gasoline of a given specific gravity and carbon content. The expression $c + d + e$ varies with each test, and represents the proportion by volume of carbon-containing gases in one cubic foot of exhaust gas.

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[7] Ratio of atomic weight of carbon to molecular weight of gas.

Computation of Pounds of Air Supplied Per Pound of Gasoline.—The pounds of air supplied per pound of gasoline is computed in the following manner:

Cubic feet of exhaust gas per gallon of gasoline ÷ (weight of 1 gallon of gasoline = 8.33 × specific gravity at 65° F.) = cu. ft. of exhaust gas per pound of gasoline = A.

A × per cent. of nitrogen in exhaust gas = total cubic feet of nitrogen supplied per pound of gasoline used = B.

B ÷ 0.79 (per cent. nitrogen in air by volume) = cu. ft. of air supplied per pound of gasoline = C.

C × 0.07572 [8] = lb. of air supplied per pound of gasoline.

Percentage Completeness of Combustion.—The percentage of the total heat of the gasoline lost due to the presence of combustible gases in the exhaust, may be calculated by either of two methods, namely, (1) the use of the quantity and calorific value of the combustible gases in the exhaust, also the calorific value of the gasoline used, and (2) the use of the analysis of the exhaust gas and gasoline.

Computation of Percentage Completeness of Combustion.—Calculation of this item by the quantity and calorific value method as applied to the average results of twenty-three cars tested on level grade is as follows:

Average Composition of Exhaust Gas, by Volume from Tests of 23 Cars, at 15 Miles per Hour Level Grade.

	Per cent.
Carbon dioxide	8.9
Oxygen	2.3
Carbon monoxide	6.3
Methane	0.9
Hydrogen	3.0
Nitrogen	78.6
	100.0

Cubic feet of exhaust gases at 65° F. and 29.92 inches Hg. = 988 (from test data).

Composition of Gasoline.

Specific gravity	0.713
Carbon, per cent.	84.3
Hydrogen, per cent.	15.7
Calorific value, B.t.u. per lb.	21,300.
Calorific value, B.t.u. per gal.	130,000.

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[8] Weight of 1 cu. ft. of air at 65° F. and 29.92 in Hg.

Exhaust gas from one gallon of gasoline on level grade tests contains:

$988 \times 0.063 = 62.2$ cubic feet CO
$988 \times 0.009 = 8.9$ cubic feet CH_4
$988 \times 0.030 = 29.6$ cubic feet H

Total heat in unburned gases per gallon gasoline:

$$\begin{array}{rcr} 62.2 \times 320[9] & = & 19{,}900 \text{ B.t.u.} \\ 8.9 \times 1000 & = & 8{,}900 \text{ B.t.u.} \\ 29.6 \times 322 & = & \underline{9{,}600 \text{ B.t.u.}} \\ & & 38{,}400 \text{ B.t.u.} \end{array}$$

$$\frac{38{,}400}{130{,}000} = 29.5 \text{ per cent.}$$

Therefore, 29.5 per cent. of the total heat of the gasoline goes out in the exhaust in the form of combustible gases—in other words, the completeness of combustion is $100 - 29.5$, or 70.5 per cent.

By gasoline and exhaust gas analysis this item is calculated directly from the exhaust gas and gasoline analysis as follows:

From gasoline analysis by weight:

$$\frac{\text{Per cent. hydrogen} \times \frac{1}{2}}{\text{Per cent. carbon} \times \frac{1}{12}} = \text{Ratio of water vapor to carbon dioxide, by volume on complete combustion} = A.$$

Assuming the heat of combustion of carbon as 14,540 B.t.u., and hydrogen as 62,000 B.t.u., then

$$\frac{14{,}540 \times \%\text{ carbon}}{(14{,}540 \times \%\text{ carbon} + (6200 \times \%\text{ hydrogen})} = \%\text{ heat units due to carbon} = B.$$

$$\frac{62{,}000 \times \%\text{ hydrogen}}{(14{,}540 \times \%\text{ carbon} + (6200 \times \%\text{ hydrogen})} = \%\text{ heat units due to hydrogen} = C.$$

From gas analysis by volume:

$$\%\,CO_2 + \%\,CO + \%\,CH_4 = \text{volume of } CO_2 \text{ formed on complete combustion} = D.$$

$$\frac{\%\,CO_2 + (0.3 \times \%\,CO)}{\%\,CO_2 + \%\,CO + \%\,CH_4} = \text{Completeness of combustion of carbon} = E.$$

$0.3 =$ Proportion of heat liberated in burning carbon to CO.

$D \times A =$ Equivalent volume of water vapor formed on complete combustion.

$$1 - \frac{\%\,H_2 + (2 \times \%\,CH_4)}{D \times A} = \text{Completeness of combustion of hydrogen} = F.$$

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[9] Gross B.t.u. per cu. ft. at 65° F. and 29.92 inches Hg.

Hence, the completeness of combustion of gasoline $= (B \times E) + (C \times F)$.

The factors A, B, and C are constant for any given grade of gasoline.

The following example explains this method:

Composition of Exhaust Gas by Volume.

	Per cent.
Carbon dioxide	9.0
Oxygen	0.5
Carbon monoxide	7.9
Methane	0.6
Hydrogen	3.7
Nitrogen	78.3
	100.0

Composition of Gasoline by Weight.

	Per cent.
Carbon	84.3
Hydrogen	15.7

Applying equations A, B, C, D, E, and F.

$$A = \frac{15.7 \times \frac{1}{2}}{84.3 \times \frac{1}{12}} = 1.12$$

$$B = \frac{14{,}540 \times 84.3}{(14{,}540 \times 84.3) + (62{,}000 \times 15.7)} = 56 \text{ per cent.}$$

$$C = \frac{62{,}000 \times 15.7}{(14{,}540 \times 84.3) + (62{,}000 \times 15.7)} = 44 \text{ per cent.}$$

$$D = 9.0 + 7.9 + 0.6 = 17.5 \text{ per cent.}$$

$$E = \frac{9.0 + (0.3 \times 7.9)}{9.0 + 7.9 + 0.6} = 65 \text{ per cent.}$$

$$D \times A = 19.6 \text{ per cent.}$$

$$F = 1 - \frac{3.7 + (2 \times 0.6)}{19.6} = 75 \text{ per cent.}$$

$$\begin{aligned}\text{Completeness of combustion} &= (B \times E) + (C \times F)\\ &= (56 \times 65) + (44 \times 75)\\ &= 69 \text{ per cent.}\end{aligned}$$

THE STABILITY OF ATOM NUCLEI, THE SEPARATION OF ISOTOPES, AND THE WHOLE NUMBER RULE.*

BY

WILLIAM D. HARKINS, PH.D.

Department of Chemistry, University of Chicago.

40. RUTHERFORD'S DIRECT EXPERIMENTAL EVIDENCE FOR THE HARKINS-WILSON THEORY OF NUCLEAR STRUCTURE.

An extremely large amount of experimental evidence in favor of the helium-hydrogen theory has been presented in the preceding 39 sections of the present paper. This evidence includes such a large number of facts that it is difficult to comprehend their importance, and even scientific men often take the unscientific attitude that a large number of facts of a varied character are not so convincing as a single fact, which is due to the difficulty of obtaining a comprehensive understanding of a great number of facts without subjecting them to an intensive study. It is therefore of interest that very simple and direct evidence in favor of the theory has been obtained by Rutherford.[42]

In their first outline of the hydrogen-helium theory Harkins and Wilson advanced the idea[43] *that the alpha particle is so extremely stable that no nucleus built of alpha particles alone—that is, no atom whose atomic weight is divisible by 4—could be expected to give hydrogen in a disintegration, but that this might be possible when hydrogen nuclei other than those contained in alpha particles are present, that is when the atomic weight is not divisible by 4.* In direct confirmation of this idea Rutherford found only four years later that in the artificial bombardment of atoms by alpha particles *hydrogen is not given off* from atoms whose atomic weight is divisible by 4, but is given off from certain light atoms whose weights are $4q+3$ and $4q+2$, if q is a whole number.

Rutherford's remarkable results depend upon the extremely high amount of kinetic energy possessed by the fast-moving alpha particles ejected from such radioactive substances as radium-C or thorium-C, which is found to be sufficient to disintegrate the nuclei of certain types of atoms. The high-speed alpha particles from thorium-C have a velocity of more than 16,000 miles per second, or about 32,000 times that of a swift rifle bullet. Thus the energy, mass for mass, is about one billion times greater than that of the bullet. When such alpha particles are shot through hydrogen, or through any compound containing hydrogen, they in some cases collide with the nuclei of hydrogen atoms, and give to the latter a velocity as high as one and six-tenths times that of the alpha particle.

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* Continued from page 535, vol. 194, October, 1922.

[42] "Artificial Disintegration of the Elements," *J. Chem. Soc.*, **121**, 400–15 (1922), Rutherford and Chadwick, *Phil. Mag.*, **42**, 809–825 (1921), **44**, 417–32 (1922).

[43] *J. Am. Chem. Soc.*, **37**, 1393 (1915), *Phil. Mag.*, **30**, 723–34 (1915).

The alpha particles from radium-C have a velocity of about 12,000 miles per second, and produce the same general effects as the ones from thorium-C. Those from the former substance have a range of 7 cm., but the range of the hydrogen nuclei with which they collide is of the order of 28 cm. and almost none of them has a range as high as 30 cm. Either the alpha particles or the swift H-nuclei may be detected by the scintillations[44] which they produce on a zinc sulphide screen, provided the latter is put within the range of the particles. While a few fast-moving hydrogen particles are detected in oxygen, it is evident that these arise from a slight contamination of the source with hydrogen.

The effect of such a contamination may be eliminated by putting the screen at a distance corresponding with a range of 30 cm., at which range no scintillations from hydrogen can be detected. However, in order to make certain that no particles from hydrogen itself or its compounds are detected, the screen was placed at a distance corresponding with a range of 32 cm. At this distance no scintillations were detected in oxygen, hydrogen, or in carbon dioxide and hydrogen mixed, but they were found when the alpha particles were shot through substances containing boron (58), nitrogen (40), fluorine (65), sodium (58), aluminium (90), or phosphorus (65). The figures in parenthesis give the forward ranges of the particles given off for the respective elements, and it is seen that these greatly exceed the range of those projected in hydrogen itself, being more than three times as great in the case of aluminium.

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[44] The paths of such H-particles are easily visible in the Shimizu-Wilson apparatus [*Proc. Roy. Soc.*, London (A) **99**, 425 (1920); *Electrician*, **86**, 720 (1921); *Engineering*, **111**, 692 (1921)] devised for making visible the tracks of alpha particles, as has been found in an experiment by R. W. Ryan and the writer, who are engaged in a photographic study of atomic disintegrations by the use of this apparatus.

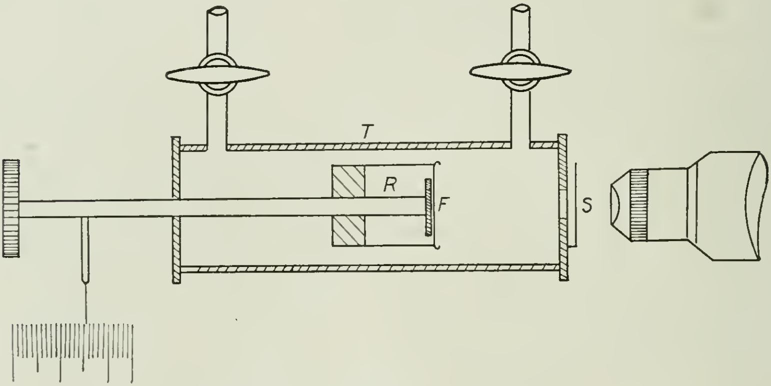
The nature of the particles ejected from these elements was determined by comparing them with the long-range particles in hydrogen, and it was found that both were deflected to the same extent in a strong magnetic field, and behaved like swift H-nuclei carrying a single positive charge. The maximum speed of the hydrogen nuclei shot off from the different atom nuclei may be calculated by assuming the law which connects the velocity and range of alpha particles according to which the velocity is proportional to the cube root of the range. The maximum speed imparted to a free H-nucleus by collision with an α-particle of velocity V has been calculated to be 1.6 V, while its range in air is about 28 cm. Accordingly the maximum velocity of the H-particle from nitrogen is 1.8 V, while that from aluminium of range 90 cm. is 2.37 V. The term " free hydrogen nucleus," as used here, refers to the nucleus of any hydrogen atom, whether in hydrogen itself or in any compound of hydrogen, but does not indicate a proton combined in any complex atom. The energy of chemical attachment is so small in comparison with that of nuclear binding, that any nucleus which is united only to planetary electrons may be considered as free in the sense of the investigation under discussion.

In a direct collision the α-particle communicates 0.64 of its energy to a free H-nucleus, and all H-nuclei which have a range greater than 56 cm. are projected with an energy greater than that of the alpha particle which ejects them, as is the case when they are driven out of phosphorus or aluminium. With the latter the maximum energy of the H-nucleus is 1.4 times that of the colliding α-particle. Thus, at least with these two atomic species, a part of the energy is derived from the nucleus which disintegrates. This is somewhat similar to what is found in the radioactive elements, where all of the energy is supposed to come from the disintegrating nucleus. In either case it is probable that a large part of the velocity and kinetic energy are gained in passing through the highly repulsive field just outside the complex nucleus.

The amount of disintegration produced in these experiments is exceedingly minute. The α-particle from radium-C passes through the planetary electronic systems of about 100,000 atoms of aluminium, but only about one particle in five hundred thousand gets near enough to the aluminium nucleus to effect the liberation of a H-nucleus. The collected α-particles from a gram of radium amount to 163 cubic millimetres of helium per year, so the amount of hydrogen liberated cannot be more than 1/1000 of a cubic millimetre per year. Thus the amount of hydrogen liberated in any practicable experiment is not detectable by ordinary chemical methods, but the disintegration may be studied by any means which will detect *individual* swift-moving H-nuclei.

The apparatus used by Rutherford in this work is extremely simple, and consists merely of a brass tube *T* (Fig. 20), 3 cm. in diameter, provided with stopcocks which permit the circulation of dry gases. At the end toward the microscope is a hole covered with a very thin silver foil. The zinc sulphide screen, *S*, is put 1.3 mm. away from the hole in order to leave room for the admission of mica screens over it. The radioactive source, *R*, is fitted at the end of a rod in order that its distance from the screen may be easily varied. Directly in front of this is fastened the substance, *F*, to be bombarded, if it is a solid. The silver foil and the mica plates are used to reduce the distance traversed by the H-nuclei. The stopping power for alpha particles of any species of atoms is proportional to the two-thirds power of its atomic number,[45] and the number of atoms per unit distance in a solid is enormously greater than in a gas; so the actual distance traversed by an

FIG. 20.



Apparatus for the scintillation method.

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[45] Glasson: *Phil. Mag.*, 43, 478 (1922).

H-nucleus, of range 28 cm. in air, is very small in a solid, particularly if the atomic number of its atoms is high. Aside from the additional convenience of a small apparatus, it is important to reduce the actual distance traversed by the alpha and H-particles as greatly as is possible, since the number of scintillations would decrease as the square of the distance between the source and the screen increases, in the case of particles of infinite range. Thus if the actual distance is 3.5 cm. the amount of radium required for the experiment is only about one-eightieth of that required at a distance of 32 cm.

A typical experiment is described by Rutherford as follows: " Suppose that the radioactive source, consisting of a brass disk coated on one side with an invisible layer of radium-C corresponding in γ-ray activity to 40 mgs. of radium, is placed 3.5 cm. from the screen and that a current of dry hydrogen is passed through the apparatus. Suppose the stopping power of the materials between the source and the zinc sulphide screen corresponds to 20 cm. of air. The passage of the α-particles, which in this case have a range of 7 cm., through the hydrogen, liberates a large number of high-speed H-atoms, which produce scintillations on the screen. Their number with the microscope described (as having a field of 40 sq. mm.) is so great—thousands per minute—that it would be impossible to count them without reducing the activity of the source. As additional screens of mica are added, the numbers fall off rapidly, and for an absorption, say, of 30 cm., not a single H-scintillation can be observed per minute. A similar effect is shown if oxygen is substituted for hydrogen, and a thin strip of paraffin wax or other hydrogen-containing substance is placed over the source. The number of H-scintillations observed for a certain absorption depends only upon the amount of hydrogen, and is quite independent of chemical combination. This is to be expected, for the forces required to set the hydrogen nucleus in rapid motion are enormous compared with the weak forces involved in chemical combination. We thus conclude that, for α-particles of range 7 cm., no H-atoms from hydrogen in the free state or in chemical combination can be detected for an absorption greater than 30 cm. of air.

" The oxygen, which gives no scintillations, is now replaced by dry air. At once for an absorption of 30 cm., we observe more than 100 scintillations per minute when for hydrogen we did not observe one. By adding mica screens we find that the scintillations cease for an absorption of 40 cm. It is clear that these particles from nitrogen have a greater range than free H-atoms, bombarded by α-rays, so the effect observed beyond 30 cm. cannot be ascribed to any hydrogen impurity in the nitrogen.

"The air is now replaced by neutral oxygen, and thin foils of say copper, iron, silver, gold, of stopping power corresponding to about 3 cm. of air, are successively placed over the source. Not a single H-atom can be observed for an absorption of 30 cm. A foil of aluminium is substituted and at once the number of scintillations jumps to more than 100 per minute. Some of the scintillations are very bright, and we find that some of the particles are so swift that the absorption must be increased to 90 cm. before the scintillations vanish."

41. DISCUSSION OF EXPERIMENTS ON ATOMIC DISINTEGRATION.

It has been seen that Rutherford's remarkable experiments, as outlined in the last section, give conclusive evidence in favor of the *Harkins-Wilson theory* of nuclear structure (1915), and are quite as conclusive in showing the invalidity of the *Rutherford theory* (1920) that the light atoms are built up largely of particles of mass 3, a theory Rutherford has now withdrawn. While the experiments show conclusively that hydrogen may be driven out of a complex nucleus, provided it is of a certain type, there still remain a number of important features of the experiments to be investigated. Some of these are listed below:

1. It is of extreme importance to determine the number of hydrogen nuclei liberated in the disintegration of a single atom such as that of aluminium or of nitrogen. The Harkins-Wilson formula for aluminium is He_6H_3, and of nitrogen, He_4H_2, which indicates the *possibility* of three hydrogen nuclei being liberated from a single atom of aluminium, and of two from an atom of nitrogen. It is of value to ask, provided more than one hydrogen nucleus is liberated, does one have a much higher speed than the others, and what are their directions? *

2. Are electrons liberated concomitantly with the protons?

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* The high energy of the emitted H-particles seems to indicate that *only one H-particle is emitted.* It may be assumed that this indicates that in the groups $p(pe)$ and $p(p_2e_2)$ the negative electrons are not able to bind firmly more than their own number of protons.

3. Are electrons emitted in any instance without the liberation of protons?

Five out of the six nuclei from which hydrogen has been driven out have the formula $a_{\left(\frac{M}{2}-\frac{1}{2}\right)} p_3e_2$, while that of nitrogen, which gives H-particles only of the shortest range, is a_3p_2e.

It is of interest to introduce here, as in the formulæ just given, the assumption that the number of alpha particles in any nucleus is equal to the *whole number* given by dividing the atomic weight of the species by 4. There is little doubt but that this is justified in general by the evidence. (It is of course *possible* that the number of protons attached in some other way is equal to as much as 4 or even more.) Consideration will now be given to the *formula-groups* which are present in the *composition* of the nuclei on the basis of this assumption. Of these p_3e_2 and p_2e_2 are relatively abundant, pe is somewhat less abundant, and p_2e and pe_2 are rare, as is indicated in Table XXVIII.

TABLE XXVIII.

Formula-Groups, Other Than the Alpha Particle, Present in the Composition of Atom Nuclei.

Group.	Disintegrated to give long-range H-particles?	Present in		Series.
		A. Present in Relatively Abundant Atomic Species.		
p_3e_2	Yes	B_1^{11}, F_1^{19}, Na_1^{23}, Al_1^{27}, P_1^{31}	(Class II)	Lithium
p_2e_2	No	Ne_2^{22}, Mg_2^{26}	(Class I)	Uranium
		B. Present in Moderately Abundant Atomic Species.		
pe	No	Be_1^{9}, Mg_1^{25}, Si_1^{29}	(Class III)	Meta-chlorine
		C. Present Only in Relatively Rare Atomic Species.		
p_2e	Yes	N_0^{14}	(Class IV)	Uranium
pe_2	No	Cl_3^{37}, K_3^{41}	(Class II)*	Meta-chlorine

* Chlorine and potassium have a higher atomic number than any atomic species thus far disintegrated, so the class number may not be in point.

Atomic species of the thorium series, that is those supposed by the theory to have nuclei built of alpha particles, or of alpha particles and cementing electrons, have not been disintegrated, so far as the experimental evidence shows. Rutherford's method, however, does not in any case *reveal* a disintegration which gives particles of a range less than 32 cm. *Thus far only those atoms* *which contain formula-groups in which the number of protons is greater than the number of electrons, have been shown to be artificially disintegrated to give hydrogen nuclei.* Even if it is proved later that atoms which show the formula-groups pe, p_2e_2, and pe_2, may be disintegrated to give hydrogen, they will be found to give particles of a shorter range, and thus exhibit less energy of disintegration, unless the present experiments are in error. Neither the p_2e group of Li_0^6 nor the p_3e_2 group of Li_1^7 has been found to give the long-range H-particles. *These facts raise the important question as to whether it is necessary for these groups to contain more protons than electrons if they are to give rise to particles of such a great range.* Unfortunately the number of cases investigated is not great enough to definitely settle this question, but the evidence thus far favors the idea that this is a necessary condition. Table XXIX lists the substances thus far investigated.

It is of interest to note that lithium, with the lowest atomic number, gave no long-range particles, and it is of importance to determine whether it disintegrates at all. The range of the particles given off is the highest for the two elements which have the highest atomic numbers of those which are disintegrated, but is much less for phosphorus than for aluminium. Elements of higher number than 31 (phosphorus) have not been found to give off long-range particles, which may be due to the higher repulsive field around the nuclei of higher charge. This does not allow the penetration of the alpha particle with the retention of such a large amount of kinetic energy; or it may be that the protons become imbedded with alpha particles as the number of the latter increases; or that in some other way the energy of attachment of the protons increases too greatly to allow them to be driven off.

A fact of the greatest interest in the case of aluminium is that nearly as many long-range H-particles are emitted in the backward as in the forward direction of the α-particles, but with a distinctly smaller velocity and range. In the case of nitrogen the chance of liberating a swift H-particle is only 1/20 that of setting a free hydrogen atom in motion.

Table XXIX B gives the distribution of the momentum between the various particles concerned in the disintegration of the atoms, as calculated by Rutherford by the use of the ordinary

laws of mechanics. The momenta are expressed in terms of the initial velocity *V* of the alpha particle. The initial momentum of the α-particle, and therefore the sum of the momenta of the three bodies, after collision, is 4 *V*. However, if more than one proton is emitted per atom, the number of bodies is greater than three. Momenta in the direction of the incident α-particle are taken as positive, those in the opposite direction as negative. The

TABLE XXIXA.

Range of the H-particles (Protons) Liberated in Rutherford's Experiments on Atomic Disintegration.

(Elements marked ". . . ." gave practically no particles of range greater than 32 cm.)

At. No.	Element.	Species.	Material.	No. of particles per minute per mg. for microscope used.	Maximum range of particles in cm. of air.*
3	Lithium	Li^{6}_{0}, Li^{7}_{1}	Li_2O	....	....
4	Beryllium	Be^{9-1}_{1}	BeO	....	....
5	Boron	B^{10}_{1}, B^{11}_{0}	B	0.15	58—38
6	Carbon	C^{12}_{0}	Co_2	....	....
7	Nitrogen	N^{14}_{0}	Air	0.7	40—18
8	Oxygen	O^{16}_{0}	O_2	....	....
9	Fluorine	F^{19}_{1}	CaF_2	0.4	65—48
11	Sodium	Na^{23}_{1}	Na_2O	0.2	58—36
12	Magnesium	Mg^{24}_{0}, Mg^{25}_{1}, Mg^{26}_{2}	MgO	....	....
13	Aluminium	Al^{27}_{1}	Al, Al_2O_3	1.1	90—67
14	Silicon	Si^{28}_{0}, Si^{29}_{1}	Si	....	....
15	Phosphorus	P^{31}_{1} and (?)	P (red)	0.7	65—49
16	Sulphur	S^{32}_{0} and (?)	S, SO_2	....	....
17	Chlorine	Cl^{35}_{1}, Cl^{37}_{3}	$MgCl_2$	....	....
19	Potassium	K^{39}_{1}, K^{41}_{3}	KCl	....	....
20	Calcium	Ca^{40}_{0}, Ca^{44}_{4}	CaO	....	....
22	Titanium	Ti^{48}_{4}	Ti_2O_3	....	....
25	Manganese	Mn^{55}_{5}	MnO_2	....	....
26	Iron	Fe^{56}_{4} (probably Fe^{54}_{2})	Fe	....	....
29	Copper	(Probably Cu^{63}_{5} and Cu^{65}_{7})	Cu	....	....
50	Tin	Sn^{116}_{16}, Sn^{117}_{17}, Sn^{118}_{18}, Sn^{119}_{19}, Sn^{120}_{20}, Sn^{121}_{21} (?), Sn^{122}_{24}, Sn^{124}_{25}	Sn	....	....
47	Silver	(Probably Ag^{107}_{15} and Ag^{109}_{16})	Ag	....	....
79	Gold		Au	....	....

* The first figure gives the forward, the second, the backward range in centimetres.

percentage energy gained from the nucleus as the result of the disintegration is given in the last column, and in terms of the initial energy of the α-particle.

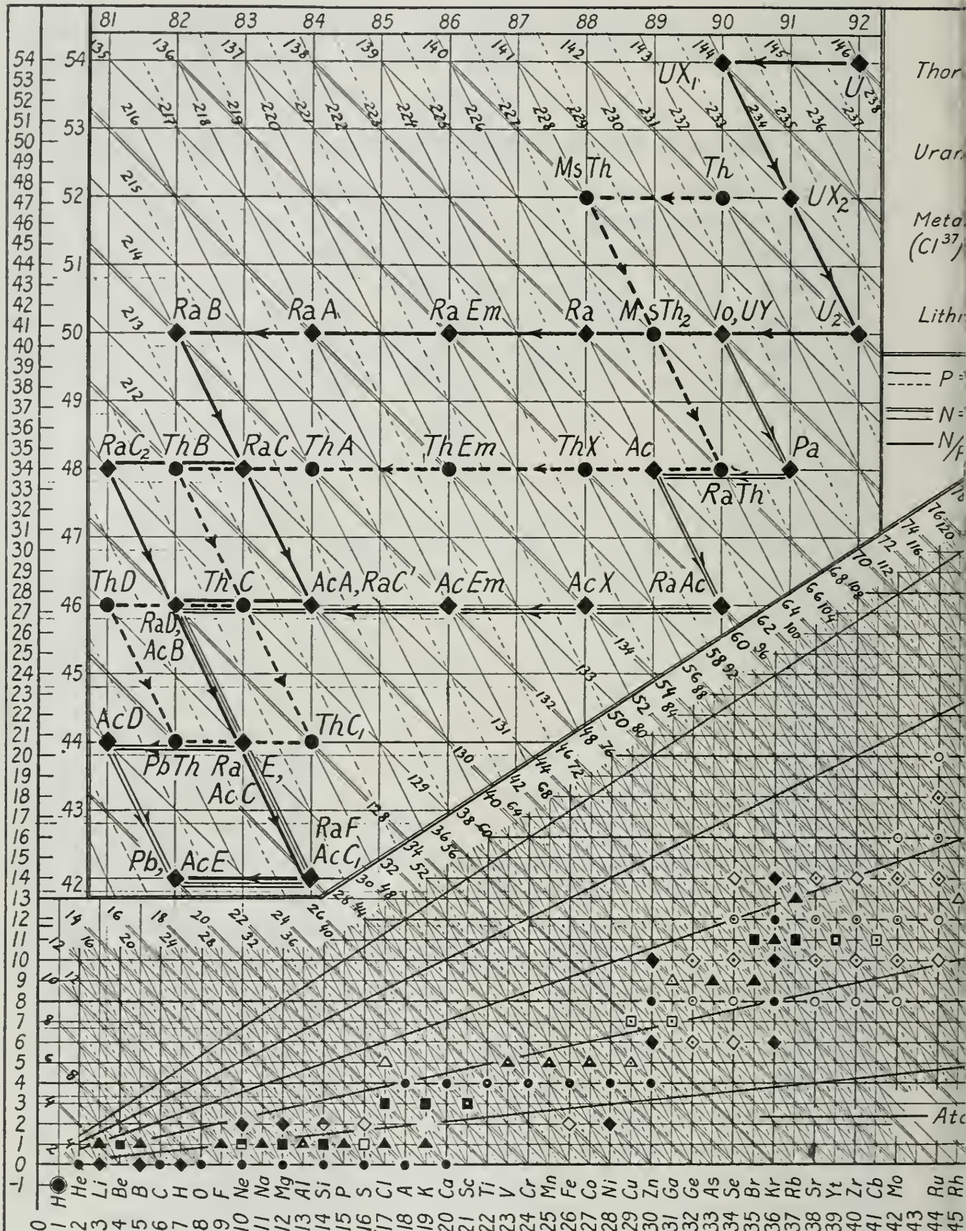
42. GENERAL PERIODIC SYSTEM OF THE ATOMIC SPECIES (ISOTOPES).

The details of the general periodic system as presented in Fig. 21, prepared for the writer by S. L. Madorsky, are of importance in the consideration of the nature of the groups present in atom nuclei. This figure plots every possible value, within the limits so far discovered, of the atomic number (X-axis), isotopic number (Y-axis), number of negative electrons (lines of slope −1) and number of positive electrons (lines of slope −2). *Every corner where all of these 4 lines meet represents a possible isotope.* This plot is of interest in that it shows very well that atomic species are found only in a relatively narrow band of the general form of a parabola. The equation of the parabola has been calculated by Professor A. C. Lunn from entirely general considerations, without paying attention to the specific data given here. The lines radiating from the origin give the values of the relative negativeness (N/P) of the nuclei. Fig. 12, already presented, represents a limited portion of the same diagram, and gives a better idea of the periodicity with respect to the atomic and isotopic numbers than the present figure, since in the latter the periodicity is obscured by the abundance of detail. However, Fig. 21 shows the periodicity with respect to the number of positive and negative electrons, which requires a very large plot for complete representation. Even numbers of negative electrons are represented by double, and odd numbers by single, lines. Of the approximately 70 atomic species, in the non-

TABLE XXIX B.

Distribution of Momentum in the Disintegration of Atoms by α-Particles.

Element.	H-particle		Residual Nucleus		α-particle.	Per cent. Gain in Energy.
	Forward.	Backward.	Forward.	Backward.		
Boron	2.02 V	−1.75 V	−0.54 V	3.23 V	2.52 V	42
Nitrogen	1.78 V	−1.32 V	1.44 V	4.54 V	0.78 V	−13
Fluorine	2.10 V	−1.89 V	−0.10 V	3.89 V	2.00 V	35
Sodium	2.02 V	−1.72 V	1.42 V	5.16 V	0.56 V	6
Aluminium	2.34 V	−2.11 V	0.78 V	5.23 V	0.88 V	42
Phosphorus	2.10 V	−1.89 V	1.14 V	5.13 V	0.76 V	15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Ra E, AcC
ThC₁
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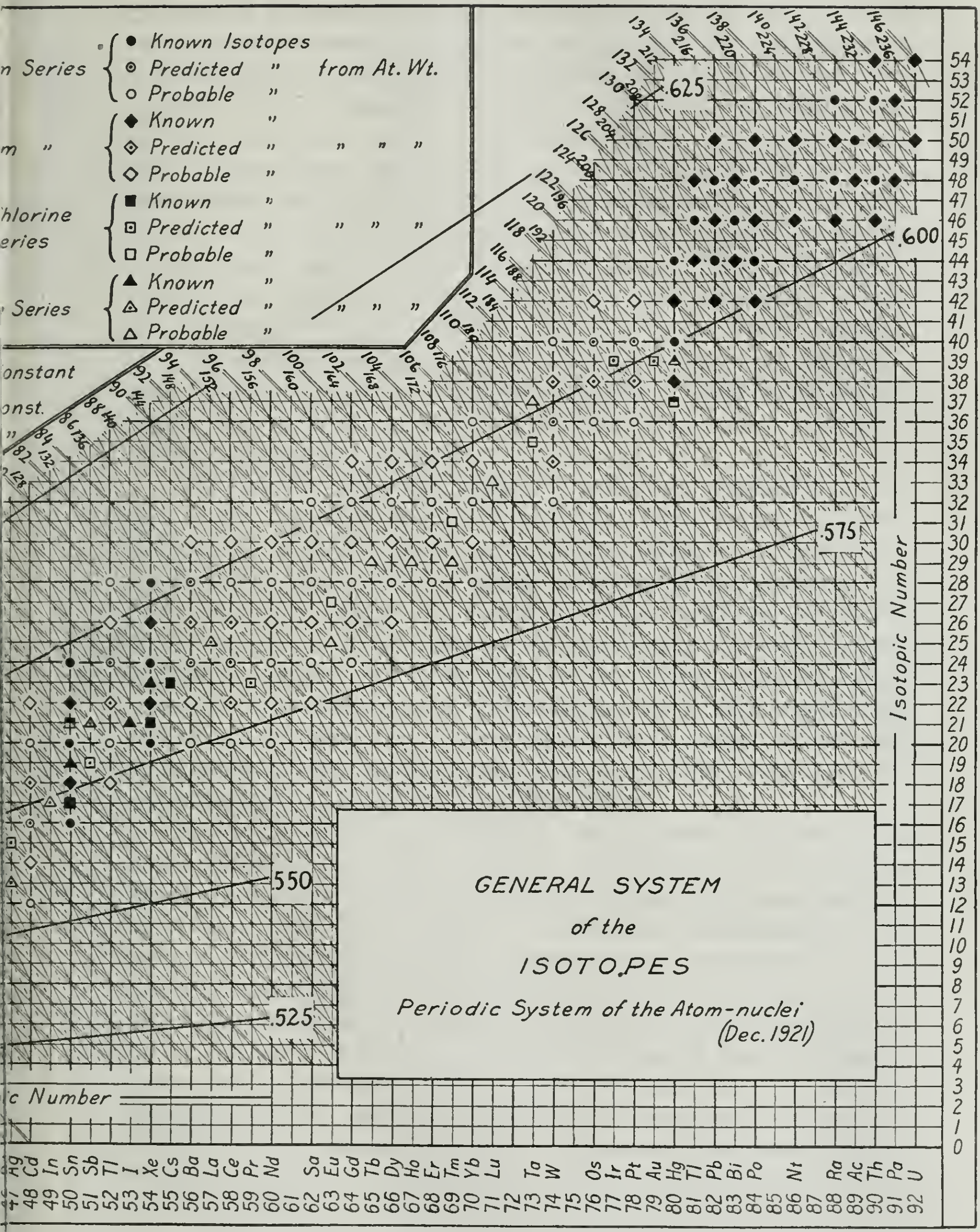
G. 21.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0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54
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radioactive portion of the plot, whose existence is almost certain, only eleven are on the single lines; in the radioactive plot (upper left-hand corner) only nine in 37 species, and these nine are very unstable. Even numbers of positive electrons are represented by solid, and odd numbers by dotted, lines. Of the 70 non-radioactive species twenty-four, or less than half, are on the dotted lines, and all of the very abundant species are on the solid lines. In the radioactive portion, every atomic species is on one of the solid, and none on the dotted lines. Thus this figure exhibits the important feature that it shows a periodicity of two in 4 different directions, with respect to (1) the atomic number, (2) the isotopic number, (3) the number of negative electrons, and (4) the number of positive electrons. These periodicities, which are summed up here, have been discussed in detail in earlier sections of the paper.

The symbols used are, with one exception, explained in the plot itself. Atomic species, which have been found by either radioactive or positive-ray methods, are inked-in. Those indicated by the latter method, whose existence seems doubtful, are half inked-in. Those not found by either method, but which lie in the region of the light atoms, and where the mean atomic weight is just that given by the Harkins-Wilson atomic weight equation, are inked-in with the exception of a very small circle in the centre. Thus far in this region every atomic species thus designated by the equation has proved to exist, whenever the experimental investigation has been made.

Positions for many predicted and probable isotopes have been designated by light outlines. A number of these, notably those for rubidium and tin, have been discovered and inked-in since they were first outlined. In the cases investigated every isotope outlined has proved to represent an actual isotope, but it is not to be expected that this will be the case in every instance. Thus when the mean atomic weight used (from the international tables) is considerably in error, it cannot be expected that the predictions will be correct. Where they are quite exact it may be expected that the isotopes predicted for elements of odd atomic number will in general be correct. No attempt has been made to designate isotopes of odd isotopic number and even atomic number, since their occurrence is not so systematic and they are of minor importance with respect to abundance. With increasing sensitiveness of the positive-ray method, it may be expected that more isotopes of this class will be discovered, and the same may be true of the species of odd atomic and even isotopic number, which are extremely rare.

43. CLASSIFICATION OF THE ATOMIC SPECIES BY SERIES.

The classification of all atomic species into 4 series, each of which naturally forms 2 classes, a principal and a secondary series, was suggested by the writer several years ago.[46] The classification is presented in Table XXX. In each case A is the principal, and B is the subordinate, series.

The relationship between the series of Table XXX and of the classes of isotopes according to section 33 is exhibited in Table XXXI.

44. HYPOTHESES IN REGARD TO THE STRUCTURE OF COMPLEX ATOM NUCLEI.

Thus far the present paper has been concerned with facts and their obvious interpretation. The subject of the structure of a complex nucleus introduces considerations of a more hypothetical nature. The model of the alpha particle already presented (Fig. 3, Section 23) represents a particle which, while it has a net charge of 2 positive, is nevertheless largely electrically negative in its exterior. Such particles, since they contain both positive and negative electrons which are not coincident in space, may act as electrical couples, and thus attract each other sufficiently to unite to form a vary stable nucleus of greater mass. In this way 3, 4, 5, 6, 7, 8, 9, or 10, but *not* 2 alone, form sufficiently stable complexes to give rise to atomic species of considerable abundance. The fact that 2 α-particles do not seem to make a stable structure, suggests that a ring or shell structure[47] of the alpha particles may be essential for stability. Thus the beryllium nucleus, if it were built up exactly according to the numerical system with respect to α-particles as holds for the other atoms of even atomic number, should consist of two α-particles (α_2), but actually its atomic weight corresponds to $\alpha_2\eta\beta$. Thus either an additional α-particle, or the group $\eta\beta$ seem

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[46] *Nature* (April, 1920), and in more detail in *J. Am. Chem. Soc.*, **42**, p. 1958 (1920).

[47] Harkins: *Physical Review*, **15**, 82 (postulate 12) (1920).

TABLE XXX.

Classification of the Atomic Species into Series.

q, *a*, and *b*, represent *any* whole numbers. E = Even No., M = At. No., n = Isotopic No.

I Thorium (Helium-Thorium) $P=4q$		II Uranium (Metaneon-Uranium) $P=4q+2$		III Lithium (Li-Co-I-) $P=4q+3$		IV (Be-Cl^{37}_{3},-Xe^{121}_{17}-Cs) $P=4q+1$	
A $M=E$ $n=4q$	B $M=\mathrm{O}$ $n=2q$ (not $4q$) $n=4q+2$	A $M=E$ $n=2q$ (not $4q$) $n=4q+2$	B $M=\mathrm{O}$ $n=4q$	A $M=\mathrm{O}$ $n=4q+1$	B $M=E$ $n=4q+3$	A $M=\mathrm{O}$ $n=4q+3$	B $M=E$ $n=4q+1$
$a_a\beta_{2b}$	$a_a\beta_{2b}\beta$	$a_a\beta_{2b}n_2\beta_2$	$a_a\beta_{2b}\eta_2\beta_2\beta$	$a_a\beta_{2b}\eta_3\beta_2$	$a_a\beta_{2b}\eta_3\beta_2\beta$	$a_a\beta_{2b}\eta\beta\beta$	$a_a\beta_{2b}n\beta\beta_2$
$\mathrm{He}2^{4}_{0}$			$\mathrm{Li}3^{6}_{0}$	$\mathrm{Li}3^{7}_{1}$			$\mathrm{Be}4^{9}_{1}$
$\mathrm{C}6^{12}$			$\mathrm{B}5^{10}_{0}$	$\mathrm{B}5^{11}_{1}$			
$\mathrm{O}8_{0}$			$\mathrm{N}7^{14}_{30}$	$\mathrm{F}9^{19}_{1}$			
$\mathrm{Ne}10^{20}_{0}$		$\mathrm{Ne}10^{22}_{2}$		$\mathrm{Na}11^{23}_{1}$			$\mathrm{Ne}10^{21}_{1}$ (?)
$\mathrm{Mg}12^{24}_{0}$		$\mathrm{Mg}12^{26}_{2}$		$\mathrm{Al}13^{27}_{1}$			$\mathrm{Mg}12^{25}_{1}$
$\mathrm{Si}14^{28}_{0}$		$\mathrm{Si}14^{30}_{2}$ (?)		$\mathrm{P}15^{31}_{1}$			$\mathrm{Si}14^{29}_{1}$
$\mathrm{S}16^{32}_{0}$				$\mathrm{Cl}17^{35}_{1}$		$\mathrm{Cl}17^{37}_{3}$	
$\mathrm{A}18^{36}_{0}$				$\mathrm{K}19^{39}_{1}$		$\mathrm{K}19^{41}_{3}$	
$\mathrm{A}18^{40}_{4}$						$\mathrm{Sc}21^{44}_{3}$	
$\mathrm{Ca}20^{40}_{0}$							
$\mathrm{Ca}20^{44}_{4}$							
$\mathrm{Ti}22^{48}_{4}$							
$\mathrm{Cr}24^{52}_{4}$				$\mathrm{V}23^{51}_{5}$			
$\mathrm{Fe}26^{56}_{4}$				$\mathrm{Mn}25^{55}_{5}$			
$\mathrm{Ni}28^{60}_{4}$		$\mathrm{Ni}28^{58}_{2}$		$\mathrm{Co}27^{59}_{5}$			
$\mathrm{Zn}30^{64}_{4}$		$\mathrm{Zn}30^{36}_{6}$					
$\mathrm{Zn}30^{68}_{8}$		$\mathrm{Zn}30^{70}_{10}$					
$\mathrm{Kr}36^{80}_{8}$		$\mathrm{Kr}36^{78}_{6}$		$\mathrm{As}33^{75}_{9}$			
		$\mathrm{Kr}36^{82}_{10}$		$\mathrm{Br}35^{79}_{9}$			
$\mathrm{Kr}36^{84}_{12}$						$\mathrm{B}\ 35^{81}_{11}$	
		$\mathrm{Kr}36^{86}_{14}$			$\mathrm{Kr}36^{83}_{11}$		
$\mathrm{Sn}50^{116}_{16}$		$\mathrm{Sn}50^{118}_{18}$		$\mathrm{Rb}37^{87}_{13}$		$\mathrm{Rb}37^{85}_{11}$	$\mathrm{Sn}50^{117}_{17}$
$\mathrm{Sn}50^{120}_{20}$		$\mathrm{Sn}50^{122}_{22}$			$\mathrm{Sn}50^{119}_{19}$		$\mathrm{Sn}50^{121}_{21}$(?)
$\mathrm{Sn}50^{124}_{24}$				$\mathrm{I}53^{127}_{21}$			$\mathrm{Xe}54^{129}_{21}$
$\mathrm{Xe}54^{128}_{20}$		$\mathrm{Xe}54^{130}_{22}$					
$\mathrm{Xe}54^{132}_{24}$		$\mathrm{Xe}54^{134}_{26}$			$\mathrm{Xe}54^{131}_{28}$		
$\mathrm{Xe}54^{136}_{28}$						$\mathrm{Cs}55^{133}_{23}$	
$\mathrm{Hg}80^{200}_{40}$		$\mathrm{Hg}80^{198}_{38}$ (?)			$\mathrm{Hg}80^{199}_{39}$ (?)		$\mathrm{Hg}80^{197}_{37}$(?)
$\mathrm{Hg}80^{204}_{44}$		$\mathrm{Hg}80^{202}_{42}$					

TABLE XXX—*Continued.*

2. Radioactive Atomic Species.

I Thorium (Helium-Thorium) $P = 4q$		II Uranium (Metaneon-Uranium) $P = 4q + 2$		III Lithium (Li-Co-I-) $P = 4q + 3$		IV (Be-Cl$^{37}_{3}$,-Xe$^{121}_{17}$-Cs) $P = 4q + 1$	
A	B	A	B	A	B	A	B
Pb82$^{208}_{44}$	Tl81$^{208}_{46}$ (ThD)	Pb82$^{206}_{42}$	Tl81$^{210}_{48}$ (RaC$_2$)				
		Pb82$^{210}_{46}$ (RaD)					
Pb82$^{212}_{48}$ (ThB)	Bi83$^{212}_{46}$ (ThC)	Pb82$^{214}_{50}$ (RaB)	Bi83$^{210}_{44}$ (RaE)				
Po84$^{212}_{44}$ (ThC$_1$)			Bi83$^{214}_{48}$ (RaC)				
Po84$^{216}_{48}$ (ThA)		Po84$^{214}_{46}$ (RaC^1)					
Nt86$^{220}_{48}$ (ThEm)	Ac89$^{228}_{50}$ (MsTh$_2$)	Po84$^{218}_{50}$					
Ra88$^{224}_{48}$ (ThX)		Nt86$^{222}_{50}$ (RaEm)					
Ra88$^{228}_{52}$ (MsTh)		Ra88$^{226}_{50}$ (Ra)	Pa91$^{144}_{52}$				
Th90$^{228}_{48}$ (RaTh)		Th90$^{230}_{50}$ (Io)					
Th90$^{232}_{52}$ (Th)		Th90$^{234}_{54}$					
		U92$^{234}_{50}$ (UII)					
		U92$^{238}_{54}$ (U)					

TABLE XXXI.

Relationship between the Classes and Series of Atomic Species.

Class I		II	III	IV
Series	Thorium A Uranium A	Lithium A Meta-chlorine A	Thorium B Uranium B	Lithium B Meta-chlorine B

to be essential to cement two α-particles together. It may be seen, however, that the evidence is not at all conclusive with respect to a ring structure, since the third particle or group may be needed merely to increase the attraction. Thus a few molecules will not form a stable raindrop, since the vapor pressure is too high, but the escaping tendency of the molecules decreases rapidly as the number of molecules increases.

When the number of α-particles increases above 10, the value of the relative negativeness (N/P) of the nucleus is too small

(0.5) to keep it stable. The simplest way in which such a nucleus may be stabilized is by the addition of two extra electrons, which would be much less firmly bound than those present in the α-particles themselves. The latter may be termed "binding electrons," while the former, one pair of which serves to attach one extra α-particle to the nucleus, may be styled "cementing electrons." In the α-disintegrations of radioactive atoms cementing, but no binding, electrons are given off. For example, the nucleus of the more stable isotope of argon (A_4^{40}) may be considered as $a_9{}^{++}(a^{++}e^-e^-)$. The group (aee), which is electrically neutral, has been designated by the writer as a "helio" group, since it has the composition, but not the structure, of a complete helium atom. The α-particle of the helio group is sometimes designated as an a' group. It will be seen that this group adds 4 to the atomic weight, and nothing to the nuclear charge or atomic number, so it is a quadruple neutron. In radioactive disintegrations the group is not emitted as a unit, but as a single α and two separate β-particles. In A_0^{36} the value of N/P is 0.500, but the addition of a helio group raises this ratio to 0.550. Proceeding from the lowest atomic numbers, argon of atomic number 18, is the first which adds on one helio group (two cementing electrons) while $Zn30_8^{68}$ is the first species to contain two helio groups (4 cementing electrons). $Kr36_{12}^{84}$ has the lowest atomic number of any species yet discovered in which the number of helio groups is 3 (6 cementing electrons), though it is probable that there is a corresponding isotope of selenium, and possibly of germanium.

The energy of formation of an α-particle from 4 protons and 2 electrons is 4.63×10^{-5} erg, a very great amount of energy when the mass involved (6.60×10^{-24} g.) is taken into account. The kinetic energy of the fastest α-particles given off in radioactive disintegrations has almost one-half as high a value as the energy of formation of the particle. Thus the energy of an α-particle from thorium-C is about 2.2×10^{-5}, while that from radium-C is about 1.2×10^{-5} erg. While the kinetic energy of such particles would not seem to be sufficient to break up an alpha particle, it would seem that it should be sufficient to disrupt some of the α-particles from more complex nuclei; particularly since the fact that atomic species whose nuclei which are complexes of

α-particles exhibit practically the same packing effect as helium itself, so that the total energy of combination of the alpha particles must be relatively small. *The greatest uncertainty in the packing effect in the union of alpha particles lies at present in the atomic weight of helium,* though this has not always been recognized in some of the recent discussions of this topic.

45. GROUPS INVOLVED IN THE DISINTEGRATION OF RADIOACTIVE ATOMIC SPECIES.

In the last section it was assumed that some of the α-particles in complex nuclei are attached by two negative electrons. Thus they contain α-particles which are converted into *neutral groups* (helio groups), and other α-particles which are not thus neutralized. In thorium there are 12 neutral to 45 non-neutral alpha particles $[45\alpha^{++} + 13(\alpha\beta\beta)^{\circ}]$.

Hypothesis 1.—Thorium disintegrates with a half-period of 1.5×10^{10} years giving off an alpha particle to form mesothorium 1, which may be

$$44\alpha^{++} + 13(\alpha\beta\beta),$$

which in turn gives off a β-particle with a period of 6.7 years, and forms

$$44\alpha^{++} + 12(\alpha\beta\beta) + (\alpha\beta)^{-}.$$

This contains a cementing electron which is not present in a neutral part, so it gives off the odd electron very quickly, with a half-period of 6.2 hours, to form

$$44\alpha^{++} + 12(\alpha\beta\beta).$$

This gives an α-disintegration with a half-period of 1.9 years. After this three more α-changes follow with constantly decreasing periods, the last half-period being 0.14 seconds. *These facts gave rise to the hypothesis*[48] *that both the alpha and the beta particles are in groups, the latter in groups of 2 and the former in groups of 1 to 10, but usually of about 4. When a group is once broken it becomes less and less stable as it becomes smaller.* (Consult the average life of radioactive atoms given in Fig. 1.)

Hypothesis 2.—In the first hypothesis it was assumed that the electrons of the helio group were, in the above-mentioned changes, given off before its α-particle, which may be designated as an α'-particle to distinguish it from other alpha particles. In the second form of the hypothesis it will be assumed that the α'-particle is given off from the neutral group before the electrons.[49]

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[48] Harkins: *Physical Review,* **15,** 88 (Feb., 1920).

According to this idea mesothorium 1 would be

$$45\alpha^{++} + 12(\alpha\beta\beta) + (\beta\beta).$$

This would give off a β-particle to form

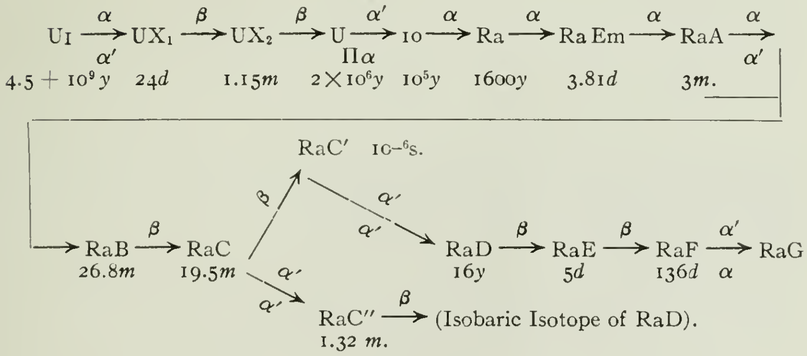
$$45\alpha^{++} + 12(\alpha\beta\beta) + \beta.$$

Since this contains a single electron not attached to any specific neutralizing group, it would readily escape, as corresponds with the low period. The two hypotheses are outlined in Table XXXII.

TABLE XXXII.

Disintegration of the Radium Series Elements According to the Two Hypotheses.

(Hypothesis 1 above, 2 below, arrows marked with an α'.)


UI $\xrightarrow[\alpha']{\alpha}$ UX₁ $\xrightarrow{\beta}$ UX₂ $\xrightarrow{\beta}$ U $\xrightarrow{\alpha'}$ IIα 10 $\xrightarrow{\alpha}$ Ra $\xrightarrow{\alpha}$ Ra Em $\xrightarrow{\alpha}$ RaA $\xrightarrow[\alpha']{\alpha}$
4.5 + 10⁹ y 24d 1.15m 2×10⁶y 10⁵y 1600y 3.81d 3m.
RaC′ 10⁻⁶s.
β
α′
α′
RaB $\xrightarrow{\beta}$ RaC
26.8m 19.5m
α′
α′
RaD $\xrightarrow{\beta}$ RaE $\xrightarrow{\beta}$ RaF $\xrightarrow[\alpha]{\alpha'}$ RaG
16y 5d 136d
RaC″ $\xrightarrow{\beta}$ (Isobaric Isotope of RaD).
1.32 m.

It will be seen that hypothesis 1 leads to a very much more consistent scheme than hypothesis 2 for the representation of the branching of the series.

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[49] The general idea of the existence of these neutral helio groups was developed by the writer in 1920 (*J. Am. Chem. Soc.*, **42**, 1958–65, 1920), without any stated preference for either of the two forms of the hypothesis given above. A year later L. Meitner (*Z. f. Physik*, **4**, 146, 1921) expressed a preference for the latter of the two possibilities. Fajans discusses this question, *Radioaktivität*, pp. 90–96 (1922).

46. STRUCTURE OF NUCLEI WHOSE ATOMIC WEIGHTS ARE NOT DIVISIBLE BY 4.

In considering the structure and composition of nuclei not built up from alpha particles (a) and electrons alone, it is important to inquire what other groups than the alpha particle may be present. Table XXXIII lists the protons (p) and electrons (e) which must be present in order to account for the atomic weights and atomic numbers of atomic species of isotopic numbers 0 to 4.

TABLE XXXIII.

Formula-Groups other than Alpha Particles Necessary to Account for the Composition of Atomic Species.

Isotopic Number.	Atomic Number.							
	Even				Odd			
	Group	Series	Class	No.†	Group	Series	Class	No.†
0	....	ThA	I	9	p_2e	UB	IV	3
1	pe	BeB	III	3	p_3e_2	LiA	II	8
2	p_2e_2	UA	I	2	$a^{++}e^{-}$	ThB	IV	0 R*
3	p_3e_3 or ep_3e_2 (?)	LiB	III	0 Kr^{83}_{11} Sn^{119}_{19} Xe^{131}_{23}	ape_2	BeA	II	3
4	ae_2	ThA	I	7	aep_2e_2	UB	IV	0 R*

* R indicates species found thus far only in radioactive disintegration series. Thus such species are extremely rare, and in general extremely unstable. Note that both types of species thus indicated belong to Class IV, and to B or subordinate series.

† The column headed "No." gives the number of atomic species of atomic numbers 1 to 28 and of isotopic numbers 1 to 5 inclusive, as shown in Fig. 12.

In considering the structural relations of the protons and electrons of these formula groups to the rest of the nucleus, it is important to keep the following facts in mind:

1. Almost all atoms contain an even number of negative electrons.
2. Most atoms contain an even number of positive electrons.
3. In atoms in which there is an odd number of negative electrons, the number of positive electrons is also almost always odd, *so there is a tendency for the positive and negative electrons to match each other in oddness or evenness.*[50] *Thus an oddness of N, when it does occur, is almost always an accompaniment of an odd value of P.*

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[50] See *Phil. Mag.*, 42 (1921), paragraph 4, p. 308 and p. 320.

Since the alpha particle contains an even number of both protons and electrons, this indicates that in the other formula-groups there is a strong tendency toward the formation of *neutral groups.*

4. In the meteorites the most abundant groups other than the α-particle, are pe, p_2e_2, and p_3e_2.

5. Thus far Rutherford has obtained long-range H-particles (protons or positive electrons) only from nuclei which contain formula-groups p_2e and p_3e_2, that is *only when there are more protons than electrons in the group.* This fact does not seem to be recognized by Rutherford himself. (Section 41, and Tables XXIX and XXX).

6. When aluminium is bombarded by α-particles nearly as many long-range H-particles are emitted in the backward, as in the forward, direction of the α-particles (Section 41).

7. H-particles are not emitted from radioactive substances, so far as is now known, and long-range H-particles have not been obtained from elements of atomic number greater than 15. This may be due to the fact that the higher positive charge of the nucleus prevents the α-particle from approaching closely enough to disrupt an H-particle, but it suggests that the protons may become more or less buried by the increasing number of α-particles.

8. Atoms with formula-groups p_3e_3 are extremely rare.

Several hypotheses as to the grouping of the protons and electrons of the formula-groups are presented below.

Hypothesis 1.—All of the negative electrons in atom nuclei, other than the binding electrons of the α-particles, serve as cementing electrons for the α-particles (or else they are attached to the part of the nucleus which contains the α-particles, without taking on the function of cementing electrons).

Hypothesis 1, A.—The protons, one, two, or three in number, form a ring, which rotates around the inner or alpha portion of the nucleus. This is the hypothesis favored by Rutherford. However, he does not give any consideration to the part played by the negative electrons of the formula-groups, and this, it may be seen, is of fundamental importance. Table XXVIII gives the formula-groups pe, pe_2, p_2e, p_2e_2, and p_3e_2, which *do not exhibit* any *simple relation between the number of electrons and protons,* and this makes it seem probable that if the protons form a ring, the electrons do not enter the ring, but attach themselves to the inner nucleus, that is, to the part built up of α-particles. These electrons would increase the relative negativeness (N/P) of the inner nucleus sufficiently to enable it to attach extra protons which form the ring. For example, in the more abundant isotopes of magnesium the nucleus contains 24 protons and 12 electrons, presumably in the form of 6 α-particles, and the value of N/P is 0.5. Now if this were to take up two electrons (possibly as cementing electrons) the value of N/P would rise to 0.583, which is higher than for any known atomic species of low atomic number. Being relatively so negative, the nucleus would add two or three protons in the form of a ring. If 2 protons, then N/P would be reduced to 0.538, and an isotope of magnesium would be formed. If 3, then N/P would be reduced to 0.519, and aluminium would be given. Both of these values of the relative negativeness correspond to a condition of stability.

The negative planetary electrons of the innermost, or K ring, seem to be held by the electrostatic attraction of the positive charge of the nucleus. In order that positive protons should be attracted, it would seem that their distance must be very much smaller, possibly within 10^{-11} cm. or less from the outer part of the inner nucleus.

Hypothesis 1, B.—The protons attach themselves to the alpha particles or negative electrons of the nucleus, but the formula-group is not associated as such. The discussion given under A would be mostly in point here.

Hypothesis 2.—Groups, other than the α-particles, which contain electrons as well as protons, are present in the nucleus. These groups need not in all cases have the composition of the formula-group, but it is not unlikely that at least a part of the groupings in the nucleus have the composition of the formula-group. Facts 3 and 5 listed above suggest that the groups p_2e and p_3e_2 may be best represented as $(pe)p$ and $(p_2e_2)p$, respectively, to indicate that the addition of a proton to the neutral groups (pe) or (p_2e_2) introduces an instability with respect to the emission of protons.

While Rutherford favors hypothesis 1, it is the opinion of the writer that hypothesis 2 is in better accord with the facts now known, since there seems to be a very marked dependence of the stability of the nucleus upon the relation between the number of electrons and protons in the formula-group, which would be very unexpected in case they are placed entirely independently as in Rutherford's hypothesis.

It would be of interest to determine if negative electrons are driven off from Cl_3^{37}, K_3^{41}, and Sc_3^{45}, which are supposed to contain the formula-group $(pe)e$. The great rarity of atoms which contain the formula-group p_3e_3 suggests that it is not unlikely that no moderately stable actual group contains more than two electrons, unless some cementing electrons are counted in. The only species now known which contain the group in question are $Kr36_{11}^{83}$, $Sn50_{19}^{119}$, and $Xe54_{23}^{131}$. These are very rare, and have positions in the system which seem to indicate that each such nucleus contains an odd or unpaired cementing electron. This would indicate that the electron-proton group in these atoms is $(p_3e_2)e$, and that the third electron acts as a cementing electron.

47. ENERGY LIBERATED IN THE DISINTEGRATION OF THE RADIOACTIVE ATOMIC SPECIES.

The mass equivalent of the energy involved in the disintegration of the various radioactive species has already been given (Section 24, Table XV). The values were calculated from data on the ranges of the particles as given in the literature in the year 1914. The table did not include the heating effect of the β and γ-rays. Table XXX gives the latest determinations of the heating effect of the principal atomic species in the radium series as taken from the work of Rutherford.

TABLE XXXIV.

Heating Effect of the Various Rays in the Disintegration of the Atomic Species of the Radium Series.

(Gram calories per hour per g. Ra)

Atomic Species.	α	β	γ	Total.
Ra	25.1			25.1
RaEm	27.6			27.6
RaA	30.5			30.5
RaB				
RaC	39.4	4.3	6.5	50.2
	123.6	4.3	6.5	134.5

The velocity of fast β-particles corresponds to what would be given them by a potential drop of about 3 million volts, that of the α-particles to 4 million volts, and the energy of the hardest γ-rays to 3 million volts.

A magnetic analysis of the β-rays of RaB shows that they give a line, as well as a continuous spectrum. According to Rutherford, Robinson, and Rawlinson[51] the lines are due to the conversion of monochromatic γ-rays in the same radioactive atom which emits them, the strong lines being due presumably to a conversion of these rays in the K ring, and the weaker lines to conversion in the L_3 ring.[52] Ellis uses the β-ray line spectrum as a means of determining the wave-lengths of short γ-rays. The shortest wave-length measured by the crystal method is 0.07 A, but many γ-rays have shorter wave-lengths than this. The new method consists in measuring the energies of different lines of the natural β-ray spectrum of the atomic species. If a certain line corresponds to the energy E_1 and is produced by a line of frequency ν, then the following quantum relation seems to hold:

$$E_1 = h\nu + w_1$$

where w_1 is the work needed to remove the electron in question to the surface of the atom. To find the frequency, all that is necessary is to determine w_1, which may be done by measuring the energy of the corresponding line in the *excited* spectrum of a substance of adjacent atomic number. In the latter case the electron will come from a corresponding level, but the energy used in removing the electron to the surface will be w_2. The difference in the energies of the corresponding β-ray lines, $E_1 - E_2$, is obviously equal to $w_1 - w_2$, and is determined directly. To find w_1 it is only necessary to see which of the corresponding levels of the two atoms differ by this amount, which may be done from the X-ray absorption data.

When sufficiently strong radioactive sources to give excited spectra cannot be obtained, the natural β-ray spectrum is analyzed by inspection. Frequently two or more lines can be found which differ in energy by the same amount as certain known levels in the atom; for example, the K and the L levels, or the $L_3L_2L_1$ levels. Table XXXV gives the wave-lengths and voltages of the γ-rays of Th D as determined by the latter method.

According to Rutherford the γ-rays are emitted from the *nuclei* of atoms, and if this is true, important information in regard to the nucleus can be obtained from such values as those given in Table XXXV.

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[51] Rutherford, Robinson, and Rawlinson: *Phil. Mag.*, 28, 281 (1914); Rutherford, *ibid.*, 34, 153 (1917).

[52] Ellis: *Proc. Roy. Soc.*, A101, 1–17 (1922).

It is possible that the β-rays given below may come partly from Th C. The energy of these rays from Th C and D mixed has been observed as high as 8×10^5 volts.

TABLE XXXV.

Wave-lengths and Corresponding Voltages of the γ-rays of ThD (At. No. = 81) as Determined by Ellis from the β-ray Spectrum.

Number.	Energy in Volts.	Wave-length in A.
1	6.54×10^5	0.0189
2	5.11	0.0241
3	2.86	0.0431
4	2.74	0.0450
5	2.54	0.0486
6	2.48	0.0498
7	2.28	0.0541
8	2.06	0.0599
9	0.560	0.220
10	0.408	0.302

Absorption Voltages of ThD (Thallium).

Ring.	Energy in Volts.	Wave-length.
K	0.869×10^5	0.1427
L_3	0.154	0.803
L_2	0.147	0.840
L_1	0.127	0.974

On the basis of Rutherford's hypothesis that the lines of the β-ray spectrum are due to a conversion of the monochromatic γ-rays in the same atom which emits the latter, Ellis concludes that the γ-rays are emitted previous to the actual disintegration of the nucleus; since Rutherford and Andrade found that Ra B, a form of lead, gives the complete *K* and *L* spectrum of lead (At. No. = 82). The principal γ-rays of Ra B correspond to energies of 2.4 to 4.0×10^5 volts, and must therefore come from within the *K* ring of planetary electrons. Chadwick[53] investigated the field of force in the region of the atom between the *K* ring and the nucleus and concluded, in accordance with the general previous opinion, that no electrons are present. If this is true, the γ-rays must come from the nucleus, as accords with Rutherford's idea.

If the γ-rays from Ra B are emitted previous to the disintegration, then, Ellis concludes, it should be possible to deduce information in regard to this nucleus from them. It is found that there is a simple arithmetical connection between the energies of the γ-rays, the first three energies being, respectively, 1.1×10^5 greater than the last three. This suggests that quantum dynamics may be used in connection with the nucleus, and indicates the five levels of Fig. 22 for the Ra B nucleus. As a consequence of the existence of these levels there should also be γ-rays corresponding to transitions from 5 to 4, 5 to 3, 4 to 3, and 2 to 1.

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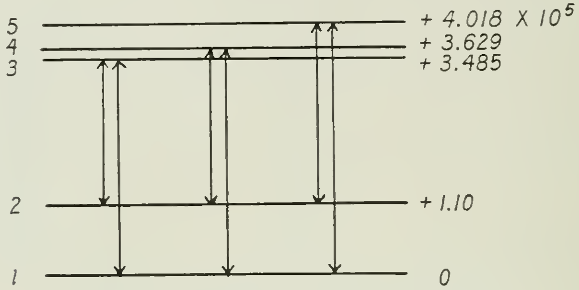
[53] Chadwick: *Phil. Mag.*, **40**, 734 (1920).

FIG. 22.



Energy levels in the nucleus of atoms of radium-B (Ellis).

Gamma rays corresponding to these energy differences were measured by the crystal method by Rutherford and Andrade, and the agreement between the observed and calculated values may be seen in Table XXXVI.

TABLE XXXVI.

Application of the Quantum Relation to the γ-Ray Spectrum of Ra B. (Ellis.)

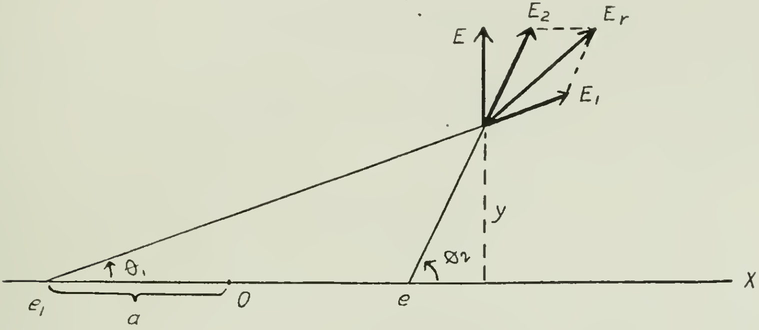
Origin.	Energy in Volts.	Wave-length in A Calculated.	Wave-length in A Observed.
5 − 4	0.389×10^5	0.318	0.324
5 − 3	0.533	0.231	0.229
4 − 3	0.144	0.857	0.853
2 − 1	1.10	0.112	0.115

It is, of course, possible that the spectrum may be emitted, not prior to, but during, the disintegration, when the change in the stationary states in the nucleus would not occur in the nucleus of a single atomic species, but in the change from one species to another. However, it seems probable that the data indicate that in the nucleus there is a fall of an electron, an alpha particle, or possibly, but not very probably, a proton, from one energy level to another.

48. CALCULATION OF THE MUTUAL ELECTROMAGNETIC MASS OF A SIMPLE SYSTEM BY PROFESSOR A. C. LUNN.

In the years 1914 and 1915, when the theory presented in the present paper was first developed, the idea was adopted that the packing effect of 0.77 per cent. involved in the change between hydrogen, on the one hand, and helium or other complex atoms, on the other, is due to a negative mutual electromagnetic mass. A general discussion of this effect has been given in Section 7 of the present paper. It seemed important to obtain a calculation which would show whether the magnitude of the loss of electromagnetic mass due to the approach of protons to electrons, could be of such a considerable magnitude as this. The problem was first attacked by E. D. Wilson, who was working with the writer, but the assistance given him by Professor Lunn amounted actually to the solution of the problem by the latter, as given below.

FIG. 23.



Let **E** be the vector of electrical intensity (Fig. 23),
H the vector of magnetic intensity,
G the electromagnetic moment,
c the velocity of light,
u the velocity of the system.

The problem thus presented for solution is the determination of the sign and the magnitude of the change of mass which results when a positive and a negative electron are brought extremely close together.

Lorentz [54] speaks of this problem, but does not solve it either with respect to the sign or the magnitude of the effect. He does state, however, that if the electrons were to be brought into immediate contact, the total energy could not be found by addition, which may be considered as equivalent to the statement that the mass of a system made up in this way would not be the same as the sum of the masses of its parts. The fundamental equations used here as the basis of the calculation which follows have been taken from the work of Lorentz.

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[54] H. A. Lorentz: "The Theory of Electrons," 1909, pp. 47 and 48. In a conversation with the writer Lorentz stated that the idea had not occurred to him of explaining the deviations of the atomic weights on the hydrogen basis from whole numbers, in this way.

The value of e, the charge on the electron, may be defined as

$$e = \iiint \rho d\tau,$$

where ρ is the volume density of the electricity, and $d\tau$ is an element of volume. For the purposes of the first part of the calculation, the electron may be considered as a point charge, but the values of the electromagnetic mass used later are given for the Lorentz form of electron, which takes the form of an oblate spheroid when in motion.

The space surrounding an electron must be considered as different from a space not adjacent to an electrical charge. If a charged particle is brought into this space it is acted upon by a force which varies from point to point, and has at every point in space a definite value and direction. This force is designated by **E**, and is a vector point function. If the electron is in motion it acts as an electric current equal to eu, where u represents its velocity. The magnetic force to this motion is easily seen to be a function of the current equivalent of the moving electron, and is also a vector, designated by **H**. Then

$$\mathbf{H} = f(\mathbf{E}, u, \phi)$$

where ϕ is the angle between **E** and the direction of motion. The direction of **H** is perpendicular to the direction of u and is at the same time circular.

It is evident that the total energy of the system is a function of both the electric and the magnetic intensities. For the purposes of this calculation the mass of a system is considered as electromagnetic, and hence as a function of the energy of the system. Therefore it is necessary to use some function of both **E** and **H**. This function is designated by **G** and is called the electromagnetic momentum.

For a field which is determined by a system of charges, the value of **G** is given as

$$\mathbf{G} = \frac{[\mathbf{EH}]}{c} = \frac{[(\Sigma_i \mathbf{E}_i)(\Sigma_j \mathbf{H}_j)]}{c} = \frac{\Sigma_i[\mathbf{E}_i\mathbf{H}_i]}{c} + \frac{\Sigma_{(ij)}[\mathbf{E}_i\mathbf{H}_j]}{c}$$

where the sum $\Sigma_{(ij)}$ is the vector product of every i with every j. The first summation gives the value of **G** which would belong to the particles provided their fields do not overlap, and the second expression which is of importance here, exhibits the effects of overlapping fields. This may be called "the mutual electromagnetic momentum." This may be designated by $\overline{\mathbf{G}}$.

For point charges

$$\mathbf{E}_1 = \frac{(1 - u^2)e_1}{4\pi r^2 (1 - u_1^2 \sin \Theta_1)^{3/2}}$$

at the point $P(x\,y\,z)$. Let

$$1 - u^2 \sin^2\Theta_1 = \beta_1^2 \text{ and } (1 - u^2) = k^2.$$

The transverse component of **E** due to the two particles 1 and 2 is

$$\mathbf{E}_t = \frac{k^2 e}{4\pi}\left\{\frac{\sin \Theta_1}{r_1^2\beta_1^3} \pm \frac{\sin \Theta_2}{r_2^2\beta_2^3}\right\}$$

where the sign is *positive* if the charges have the same sign, and *negative* if they are of opposite sign. As only the longitudinal component of the vector **G** is desired, only the transverse component of **E** is needed.

$$\mathbf{H} = \frac{u}{c}\,\mathbf{E} \sin \phi$$

where ϕ = angle between **E** and the direction of u. If $\mathbf{E}_t$ is used $\phi = 90°$. Therefore

$$H = \frac{u}{c}(E_1 \sin \Theta_1 \pm E_2 \sin \Theta_2)$$

$$G_L = \frac{[E_t H]}{c} = \frac{u}{c}(E_1 \sin \Theta_1 \pm E_2 \sin \Theta_2)^2$$

and

$$\overline{G} = \pm \frac{2u}{c^2}\int E_1 E_2 \sin \Theta_1 \sin \Theta_2 \, d\tau$$

$$= \pm \frac{2u}{c^2}\frac{k^4 e^2}{(4\pi)^2}\int \frac{\sin \Theta_1 \sin \Theta_2}{r_1^2\, r_2^2\, \beta_1^2\, \beta_2^3}\, d\tau$$

$$d\tau = 2\pi y\, dy\, dx$$

$$\sin \Theta_1 = \frac{y}{r_1} \qquad r_1^2 = (a+x)^2 + y^2 \qquad r_2^2 = (x-a)^2 + y^2$$

$$\beta_1^2 = 1 - u^2\left(\frac{y}{r_1}\right)^2 = \frac{r_1^2 - u^2 y^2}{r_1^2}$$

$$r_1^2 \beta^2 = r_1^2 - u^2 y^2 \text{ and } r_1 \beta_1 = (r_1^2 - u^2 y^2)^{1/2}.$$

Thus

$$\bar{G} = \pm \frac{2u}{c^2}\,\frac{k^4e^2}{(4\pi)^2}\int_0^{\infty} dx \int_{-\infty}^{+\infty} dy\,\frac{2\pi y^3}{(r_1\beta_1 r_2\beta_2)^3}$$

$$= \pm \frac{uk^4e^2}{8\pi^2c^2}\,2\,(2\pi)\int_0^{\infty} dx\int_0^{\infty} dy\,\frac{y^3}{\{[(x+a)^2+(1-u^2)y^2]\,[(x-a)^2+(1-u^2)y^2]\}^{3/2}}$$

If

$$(x+a)^2 = a = x^2 + 2ax + a^2$$

$$(x-a)^2 = \beta = x^2 - 2ax + a^2$$

$$a - \beta = 4ax$$

$$y^2 = z \quad y^4 = z^2 \quad 4y^3dy = 2zdz$$

then

$$\bar{G} = \pm \frac{uk^4e^2}{2\pi c^2}\,J,$$

where

$$J = \int_0^{\infty} dx \int_0^{\infty} \frac{y^3dy}{\{[\alpha+k^2y^2]\,[\beta+k^2y^2]\}^{3/2}} = \frac{1}{2}\int_0^{\infty} dx\int_0^{\infty}\frac{zdz}{\{[a+k^2z]\,[\beta+k^2z]\}^{3/2}}$$

$$= \frac{1}{2}\int_0^{\infty} dx \int_0^{\infty}\frac{zdz}{[\alpha\beta + (\alpha+\beta)\,k^2z + k^4z^2]^{3/2}}$$

$$= \frac{1}{2}\int_0^{\infty} dx\left[\frac{2\,(\alpha+\beta)\,k^2z + 4\,\alpha\beta}{(\alpha-\beta)^2k^4\sqrt{\alpha\beta+(\alpha+\beta)\,kz+k^4z^2}}\right]_0^{\infty}$$

$$= \frac{1}{2}\int_0^{\infty} dx\left[\frac{2\,(\alpha+\beta)\,k^2}{(\alpha-\beta)^2k^4k^2} - \frac{4\,\alpha\beta}{(\alpha-\beta)^2k^4\sqrt{\alpha\beta}}\right]$$

$$= \frac{1}{2}\int_0^{\infty} dx\left[\frac{2}{(\alpha-\beta)^2k^4}\right]\left[\alpha+\beta-2\sqrt{\alpha\beta}\right]$$

$$= \frac{1}{k^4}\int_0^{\infty}\left(\frac{\sqrt{\alpha}-\sqrt{\beta}}{\alpha-\beta}\right)^2 dx + \frac{1}{k^4}\int_0^{\infty}\frac{dx}{(\sqrt{\alpha}+\sqrt{\beta})^2}.$$

If

$$x < a \quad \sqrt{\beta} = \alpha - x. \quad \text{If } x > \alpha, \quad \sqrt{\beta} = x - a$$

then

$$J = \frac{1}{k^4}\left[\int_0^{a}\frac{dx}{[(x+a)+(x-a)]^2} + \int_a^{\infty}\frac{dx}{[(x+a)+(x+a)]^2}\right]$$

$$= \frac{1}{k^4}\left[\int_0^{a}\frac{dx}{4a^2} + \int_a^{\infty}\frac{dx}{4x^2}\right]$$

$$= \frac{1}{4k^4}\left\{\frac{1}{a^2}\Big[x\Big]_0^{a} + \Big[-\frac{1}{x}\Big]_a^{\infty}\right\}$$

$$= \frac{1}{4k^4}\left\{\frac{1}{a} + \frac{1}{a}\right\}$$

$$= \frac{1}{2ak^4}.$$

Accordingly

$$\overline{G} = \pm \frac{uk^4e^2}{2\pi c^2}\frac{1}{2ak^4}$$
$$= \pm \frac{ue^2}{4ac^2\pi}.$$

The mass represented by this value of $\overline{G}$ is

$$\Delta m = \pm \frac{e^2}{4\pi c^2 a}\cdot \tag{1}$$

Now the longitudinal mass m_1 is

$$m_1 = \frac{e^2}{6\,c^2R} \tag{2}$$

where R is the radius of the electron.

By division of (1) by (2)

$$\frac{\Delta m}{m} = \frac{3R}{d} \tag{3}$$

Equation 1 gives the effect of electromagnetic mass, which appears as a "packing effect" equal to 0.77 per cent. of the total mass. For a discussion of this effect reference should be made to Section 7.[55]

Expressed in ordinary units, the above equations become:

$$\Delta m = \frac{2e^2}{c^2d} \tag{1}$$

and

$$m = \frac{2e^2}{3c^2R} \tag{2}$$

The total mass of a proton and an electron is

$$m_{pe} = \frac{2}{3c^2}\left\{\frac{e^2}{R} + \frac{e^2}{r} - \frac{3e^2}{d}\right\}$$

This equation was derived independently by Nicholson, but he did not apply it to explain the packing effect.[56]

49. ON THE EXISTENCE OF ALPHA PARTICLES IN COMPLEX NUCLEI.

The evidence given in the present paper shows conclusively either (1) that the nuclei of complex atoms *contain* α-particles, or that if they do not contain them they certainly (2) have been built from α-particles, and on the whole favor the idea that both of these are true. The fact, first pointed out by the writer in 1915, that the heavier atoms exhibit practically the same packing effect (0.76 per cent.) as the helium atoms, and Rutherford's experiment as well, seem to be very strongly in favor of the view that α-particles are actually present. Brosslera[57] favors the idea that the mean packing is equal to that of the α-particle, but that the arrangement of electrons and protons is not the same as it is in such particles. Evidently, however, he is not familiar with much of the evidence presented here.

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[55] By a typographical error equation 1 is given incorrectly in this section.

[56] Presented in a paper to the Physical Society, Feb. 26, 1915.

50. THE NUCLEAR AND NON-NUCLEAR PROPERTIES OF ATOMS EXHIBIT PERIODICITIES WHICH ARE ENTIRELY DIFFERENT.

According to the current view the nucleus is very minute in comparison with the space occupied by the non-nuclear system of negative electrons. In agreement with this idea, the characteristics of the nucleus have been found to be independent of the non-nuclear system. One of the best evidences that this is true is found in a comparison of the ordinary, or Mendelejeff periodic system of the elements (Fig. 24 presents one of its latest forms), which relates to the system of planetary electrons, with that of the atomic species developed by the writer, and described in the present paper (Fig. 21, and Figs. 8, 9, and 10). The two sets of figures show no resemblance in the periodicities which they exhibit. Table XXXVII shows that the periods in the chemical system are 2, 8, 18, or 32 elements in length.

TABLE XXXVII.

Periodicity of the Physical and Chemical Properties of the Elements (Planetary System of Electrons.)

	Cycle 1.		
Period 1.	First very short period	H–He	$= 2 = 2 \times 1^2$ elements.
	Cycle $2 = 4^2$ elements.		
Period 2.	First short period	Li–Ne	$= 8 = 2 \times 2^2$ elements.
Period 3.	Second short period	Na–A	$= 8 = 2 \times 2^2$ elements.
	Cycle $3 = 6^2$ elements.		
Period 4.	First long period	K–Kr	$= 18 = 2 \times 3^2$ elements.
Period 5.	Second long period	Rb–Xe	$= 18 = 2 \times 3^2$ elements.
	Cycle 4.		
Period 6.	First very long period	Cs–Nt	$= 32 = 2 \times 4^2$ elements.
Period 7.		Eka-Cs–U	incomplete.

Fig. 25 shows the same periodicity in some of the physical properties; compressibilities, atomic volumes, coefficients of expansion, and melting points—when plotted against the atomic number. All of these relate to the planetary system of electrons.

A number of physicists have recently ascribed the magnetic characteristics of substances to the nuclei of atoms, but a glance

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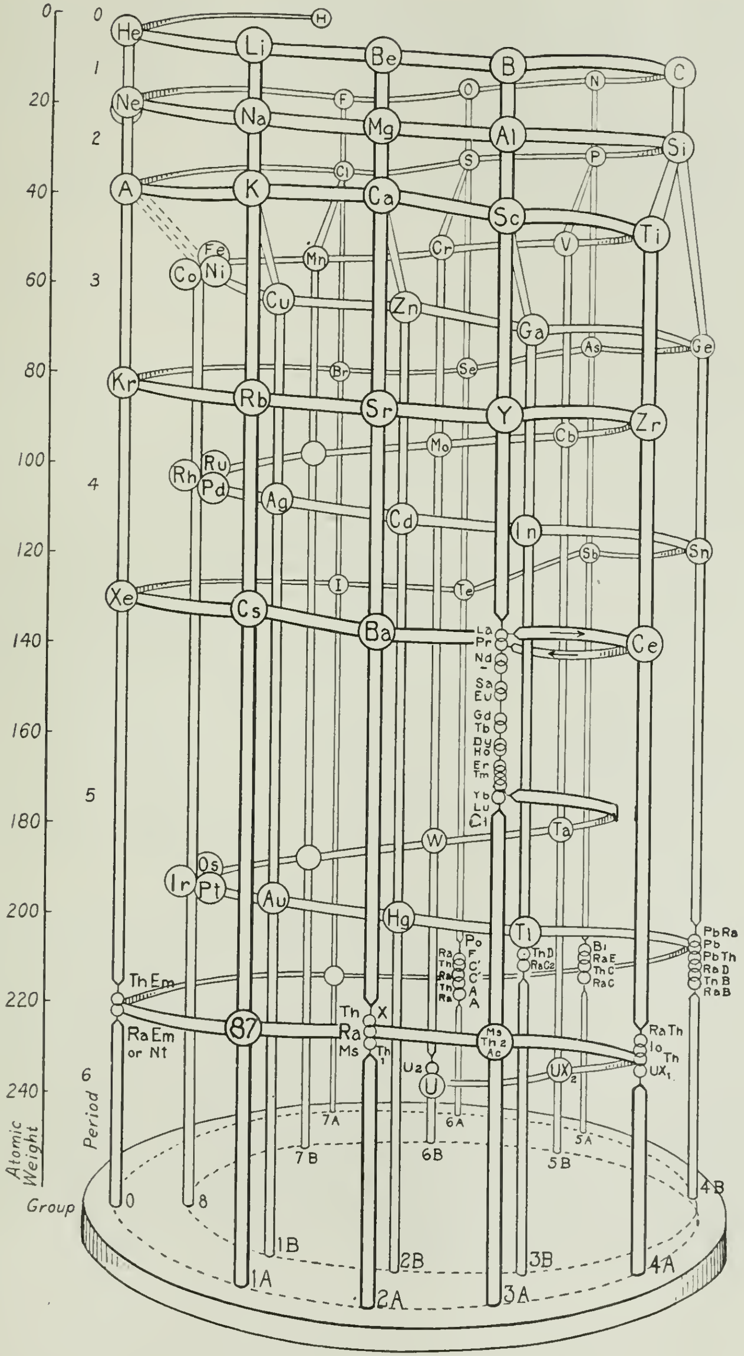
[57] *Rev. Chim.*, 1, 42, 74 (1921).

FIG. 24.

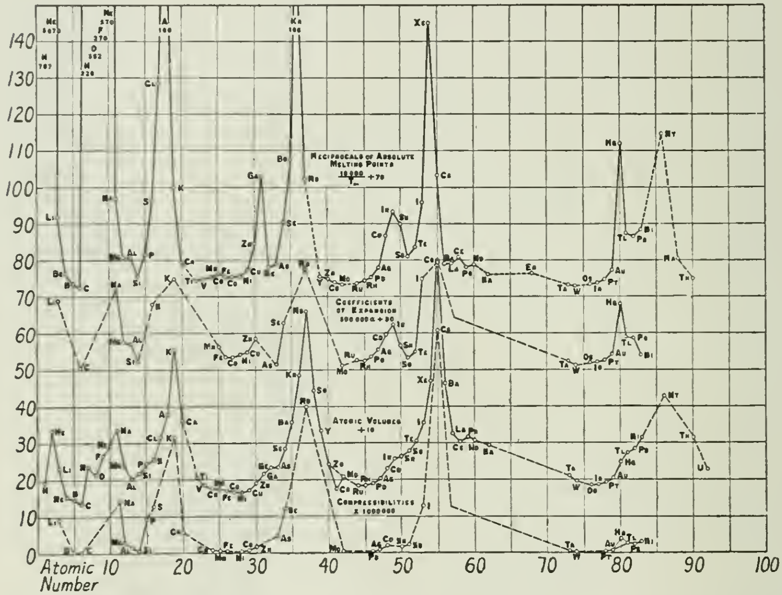


Periodic table by W. D. Harkins.

at Fig. 26, which plots the specific magnetic susceptibilities of the elementary substances against the atomic number, shows that there is considerable resemblance to Fig. 24, but none to any form of figure which represents nuclear *periodicities,* so at least the variation of the magnetic properties is caused by the variation in the planetary system.

Fig. 27 shows that in an α-change, in which the loss of atomic weight is 4, the group number is decreased by 2; while in a β-change, in which the atomic weight remains constant, the group number is increased by one. This is known as the displacement rule of Soddy, Fajans, and others. Evidently in the loss of an α^{++}-particle the nucleus loses two of its net positive charges, so the number of planetary electrons which it can hold is reduced by 2. Since the nucleus has a very high-speed recoil it travels so fast that it loses more than 2 of its planetary electrons, so the recoil atom is positive. This positive ion then picks up electrons until it becomes neutral. The neutral atom thus formed contains two less electrons in its outer or valence shell, than it had before it lost the alpha particle.

Fig. 25.

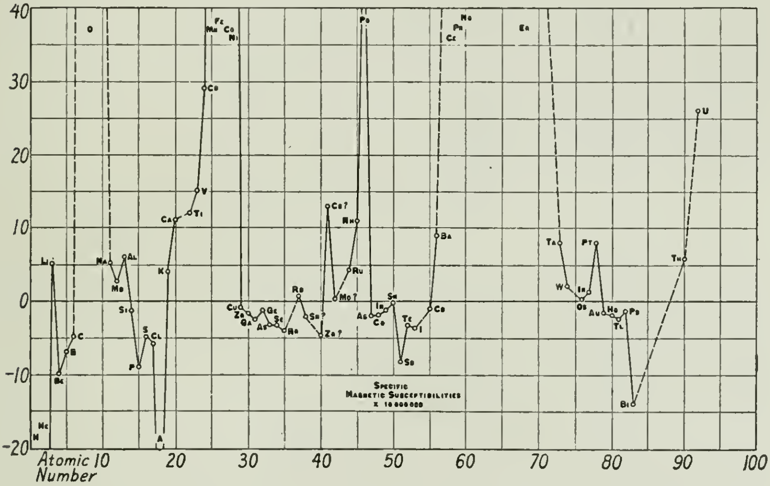


In a β^--change the nucleus loses a negative charge, which means a gain of one in its net positive charge. As a result the nucleus can hold one more negative electron in the neutral atom, so one outer or valence electron is picked up.

51. SLIGHT DIFFERENCES IN THE SPECTRA OF ISOTOPES, WHICH INDICATE: (1) MINUTE DIFFERENCES IN THEIR CHEMICAL PROPERTIES, AND (2) THAT EITHER THE NON-COINCIDENCE IN SPACE OF THE CHARGES OF THE NUCLEUS, OR ITS MASS, GIVE RISE TO A FORCE WHICH ACTS ON THE PLANETARY ELECTRONS.

Ordinary lead of atomic weight 207.20, and lead from radium (Ra G), of atomic weight 206.318, have been found to exhibit a difference of 0.0044 A. in the line λ4058. This amounts to slightly more than one-millionth or 0.0001 per cent. of the total wave-length.[58] The discovery of this shift is of particular interest, since at least 7 careful experimental investigations made previously had led to the conclusion that the spectra of isotopes are identical.

FIG. 26.



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[58] Harkins and Aronberg, *Proc. Nat. Acad. Sci.*, 3, 710–15 (1917); Aronberg, *Astrophys. J.*, 47, 96–103 (1918); Harkins and Aronberg, *J. Am. Chem. Soc.*, 42, 1328–1335 (1920). The spectroscopic work was done by Aronberg, and its success was due largely to the suggestions of Professor H. G. Gale. The shift has been confirmed, both with respect to its magnitude and direction, by Merton [*Proc. Roy. Soc. of London*, **96A**, 388–95 (1920)]. The radium-lead was supplied by Professor T. W. Richards.

These investigations were as follows: Those of Russell and Rossi,[59] and of Exner and Haschek,[60] using thorium and ionium; that of Aston [61] on the isotopes of neon; that of Soddy and Hyman [62] on lead from thorium and ordinary lead, and finally those of Richards and Lembert,[63] Hönigschmidt and St. Horivitz,[64] and of Merton,[65] on radium G and ordinary lead. Merton used a grating, and finally a Fabry and Perot étalon, and concluded from his work with the latter that there is no difference in wave-length as great as 0.003 A. for the line λ4058 in the spectrum of ordinary lead and of radium-G.

However, it should be noted that most of these investigators were precluded from the discovery of the shift in question by the lack of sensitiveness of the spectrographs at their command, whereas in the work in Chicago the Michelson 10-inch grating with a 30-foot Littrow mounting was used in the sixth order.

The shift found experimentally is 100 times greater than that predicted by Bohr's equation [66]

$$v = \frac{2\pi^2 e^2 E^2\, mM}{h^3\,(M+m)}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

and enormously greater than that indicated by the simple gravitational theory. The discovery of the effect was brought about by the idea of the writer that there should be a slight difference in the spectra of isotopes other than the extremely simple mechanical effect suggested by Fowler [67] and given in Bohr's equation. First, differences in the placing of the positive and negative electrons inside the nucleus should make the attractive force between an electron and the nucleus different in different isotopes, although it seemed not unlikely that this might produce such a small effect in the spectral lines as to make its detection impossible. Second, it seemed not improbable that at such a minute distance as that between a nucleus and a planetary electron, the mass of the nucleus might attract the electron much more greatly than corresponds to the simple inverse square law; particularly if gravitation has an electromagnetic origin.

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[59] *Proc. Roy. Soc. (London)*, 87, 478 (1912).

[60] *Sitz. Akad. Wiss., Wien (Abt. IIa)*, 121, 175 (1912).

[61] *Brit. Assoc. Meeting*, 1913, p. 403.

[62] *J. Chem. Soc.*, 105, 1402 (1914).

[63] *J. Am. Chem. Soc.*, 36, 1329 (1914).

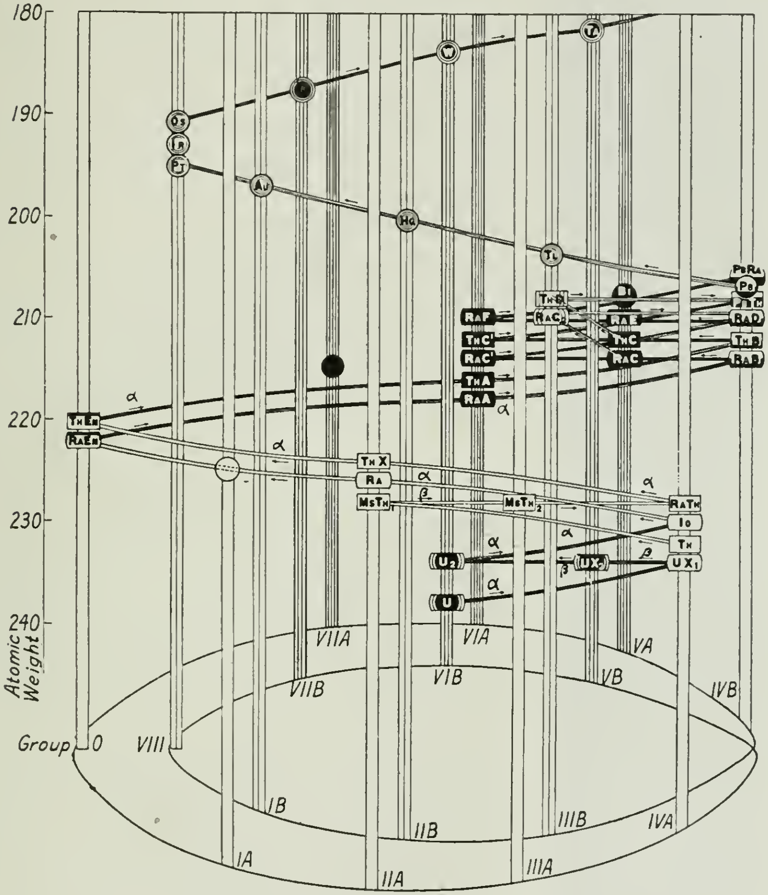
[64] *Sitz. Akad. Wiss., Wien (Abt. IIa)*, 123, Dec. (1914).

[65] *Proc. Roy. Soc. (London)*, 91, 198 (1914).

[66] Bohr: *Nature*, 92, 231 (1913).

[67] Fowler: *Nature*, 92, 95 (1913).

FIG. 27.



Periodic system of the elements radioactive portion.

The source of light used was a lead arc in a vacuum of 0.04 mm. pressure of lead vapor. Such an arc was used first, but with other metals, by Wali-Mohammed. The current was 1.1 amperes and the voltage 40, but a variation in the voltage and current was found to produce no change in the position of the lines. Fig. 24 is a diagram of the apparatus used. The anode of lead was held in place by a porcelain tube. Two such arcs, one containing ordinary and the other isotopic lead, were run side by side at the same pressure, and the spectrum of both samples was taken at the same time on the same plate. The position of the spectra on the plate, the tubes in which the arcs were placed, and the samples of lead were interchanged frequently, with the result that the shift always followed the lead, and was not affected by instrumental changes.[68]

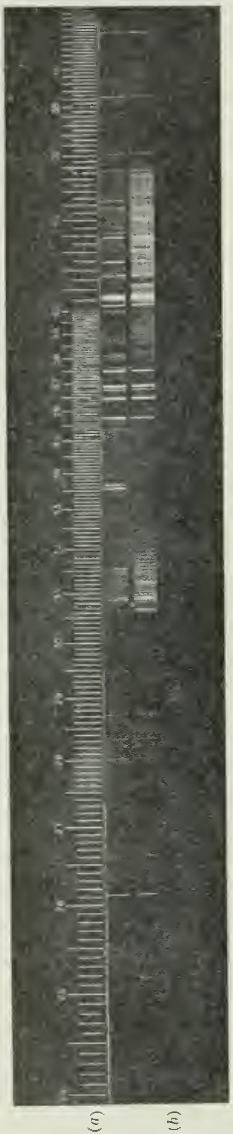


FIG. 28.

[Spectrum of lead (*a*) and radio-lead (*b*).

It is of interest that *the electron in the heavier atom always gave the greater frequency, as would be predicted from theory if it is the additional mass in the nucleus which produces the effect.*

Thus there has been discovered an effect upon the vibration of an electron, the most apparent cause of which is the change in the mass of the nucleus of an atom, which must then be accompanied with a change in the force acting upon the electron, otherwise the vibration period of the latter would not be changed.

Fig. 28 shows the spectrum of lead from radium and ordinary lead as taken on an ordinary spectrograph, which shows them to be identical except for the effects of impurities. The lead used in the experiments with the grating was very much more highly purified than that from which the photograph was obtained. The dispersion used with the grating was so high that few lines were found on the plate.

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[68] Merton [*Proc. Roy. Soc. London,* **96A**, 388–95 (1920)] has confirmed the experimental results both with respect to magnitude and sign.

52. NON-IDENTITY OF ISOTOPES IN CHEMICAL PROPERTIES.

The slight differences found in the vibration frequencies of the light given off by isotopes indicates that the electrons are not held by identical forces, *so isotopes should not be identical from the chemical standpoint,* though the minute difference found in wave-length (0.0001 per cent.) shows clearly that the chemical means now available are not capable of detecting the difference in the properties of the isotopes of lead. It is quite possible, when the difference in mass of the isotopes is as high as 16 per cent., as is the case with Li^6 and Li^7, that the chemical differences would be sufficient to be apparent to the most delicate tests. This evidently depends upon how the magnitude of the effect varies with the mass of the nucleus, which is at present entirely unknown.

Richard's [69] has shown in very precise experiments that the atomic volumes and melting points of ordinary lead and lead from radium are the same within the limits of the experimental errors. *The wave-length of the spectrum lines is the first chemical property with regard to which isotopes have been found to differ.*

53. SPECTRA AS A MEANS OF DISTINGUISHING BETWEEN ISOTOPES.

It is evident, if isotopes give slightly different spectra, that they may be distinguished by the use of delicate spectroscopic apparatus. It might seem also that the presence of isotopes in a mixture might be thus detected, but the latter supposition was not found justified in the case of lead, though it may be by later work on lighter isotopes. Both specimens of lead gave a line of about the same width, and this line was shifted as a whole, a remarkable result if ordinary lead is, as it is usually supposed to be, a mixture of isotopes of atomic weights 206 and 208. Also, even if ordinary lead should be an individual isotope, the radium lead used contained about 30 per cent. of ordinary lead, so on the basis of either hypothesis a mixture was used.

(*To be concluded.*)

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[69] T. W. Richard's "Presidential Address to the American Association for the Advancement of Science" (1918), *J. Am. Chem. Soc.*, 38, 221 (1916).

The Yield of Glucose from Cotton Cellulose.—IRVINE and HIRST (*J. C. S.*, 1922, vols. 121–2, 1885) made an investigation with a view of determining the reason that the usual processes for converting cellulose into glucose do not give the yield that would be expected upon the theory that cellulose is composed entirely of glucose units. Previous investigations by Irving and Soutar in 1920 had given a yield of 85 per cent. The experiments now reported were carried on upon the same general principles as the former ones, but a notable improvement was obtained by conducting the acetolysis in the manner suggested by Barnett (*J. S. C. I.*, 1921, v. 40). An excellent yield of cellulose triacetate of uniform quality was obtained, and as no sugar was found in the washings, much work was eliminated. The conversion of the acetate into methylglucoside was performed in many ways, but for quantitative work of this kind, the best results were obtained by digesting small amounts of the compound with methyl alcohol containing about 0.75 per cent. hydrogen chloride. The use of an autoclave was abandoned, the whole procedure being carried out in sealed tubes, containing about 4 grams of the triacetate. After about seventy hours' action only a trace of solid matter remained, and the solution, which was faintly yellow, contained alpha- and beta-methylglucosides in equilibrium. The specific rotation of the liquid ranged within 107–108°, the calculation being based on the assumption that the whole of the cellulose has been converted into the methylglucoside.

Each of the reactions involved has been carried out on numerous occasions and by independent workers. With practice and experience the yields have been regular, and the following figures are submitted as the average of the concordant experiments:

Cotton cellulose	100 parts
Cellulose triacetate	117 parts
Methylglucosides	114.1 parts
Equivalent of glucose	106 parts

The yields are in each case about 99.5 per cent of the theoretical.

H. L.

Minimum Sound Energy for Audition for Tones of High Frequency. C. E. LANE. (*Phys. Rev.*, May, 1922).—For frequencies ranging from 2000 to 14,000 per second it was found that, in order to produce the sensation of sound there must flow through a square centimetre in a second an amount of sound energy equal to 7×10^{-8} ergs. This quantity is practically the same for the range of frequencies specified, though small differences exist not only between individuals but even between the two ears of the same person. Above 14,000 per second more and ever more energy is needed for the production of the sensation until, at some frequency between 18,000 and 20,000, according to individual idiosyncrasy, 1,400,000 times as much energy as was adequate at the lower pitch does not produce any sensation. This upper frequency limit is highest for children and lowest for old people.

G. F. S.

NOTES FROM THE LABORATORY OF PURE SCIENCE, NELA RESEARCH LABORATORIES.*

SHORT ELECTRIC WAVES.

By E. F. Nichols and J. D. Tear.

[ABSTRACT.]

THE present experiments were undertaken in the hope that by devising improved instruments and better and more accurate methods for experimenting with short electric waves, further progress might be made in narrowing the still unexplored region of the spectrum which extended from a wave-length of 0.3 mm. to one of about 10 mm., and in making the results of future short electric wave experiments more nearly quantitative and trustworthy.

The source of radiation finally adopted is a modified form of Hertzian doublet, embodying a number of new features making possible the generation of very short waves. A disruptive discharge is caused to pass between two tungsten cylinders immersed in kerosene. The cylinders, of which the smallest used were 0.2 mm. long and 0.2 mm. in diameter, were held in place by being sealed into the closed ends of hard glass tubes which were mounted with micrometer adjustments, enabling the spark gap between the two halves of the doublet to be accurately controlled. High potential leads enter through the glass tubes and are brought within a few millimetres of the outer ends of the tungsten cylinders, leaving short air gaps for the discharge to cross. Streams of compressed air keep these air gaps deionized and free from oil and also serve to cool the glass-tungsten seal. When the gap in oil between the two cylinders is of the proper length (about .01 mm.) each discharge sets up electrical oscillations in the doublet, causing it to emit a highly damped radiation, the fundamental wave-length of which is determined by the dimensions of the doublet and by the dielectric constants of the surrounding media, *i.e.*, oil and glass. In practice the fundamental wave-length emitted by the doublet was found to

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* Communicated by the Director.

be from three to five times the overall length of the doublet, the larger factor applying to the smaller doublets.

The source is mounted on an optical bench at the principal focus of a paraffin lens. The radiation emerging from this collimating lens in a beam of parallel rays passes through the interference apparatus or whatever optical system is in use at the time, and is then collected by a second lens and brought to a focus upon the vanes of the receiving instrument.

By adapting the Nichols radiometer to electric wave reception an enormous increase in sensitivity over earlier electric wave receivers has been obtained. This increased sensitivity is due in part to the particular receiving elements chosen for the resistance-absorption of the incident radiation; in part to the substitution of the radiometer method for the less direct thermocouple galvanometer method of measuring small amounts of energy; and again in part to further improvements in radiometer technic. A number of minor changes in the form of radiometer suspensions have been made, and a considerable decrease in weight has been achieved, making possible the use of much finer quartz fibres. The total weight of some of the smaller suspended systems was about 0.5 mg.

Receiving elements, either of 1μ platinum wire of proper length for resonance with the incident radiation, or of metallic films deposited upon thin mica strips or quartz fibres by the evaporation method, are substituted for the usual blackened radiometer vanes. Thin mica shields are so mounted about 0.1 mm. in front of or behind the receiving elements as to make the radiometer action of the two vanes unilateral.

Wave-length measurements were made with the Boltzmann mirror interferometer and also with a reflecting echelon or flight of steps, made of carefully machined brass blocks so mounted as to be easy of adjustment to any desired spacing, width, or thread. The echelon was also used for obtaining an approximate analysis of the radiation emitted by the Hertzian doublet and to separate out more homogeneous radiation of a desired wave-length.

By the foregoing procedure electric waves from several centimetres down to 1.8 mm. in length have been isolated. Under favorable conditions a wave-length of 0.8 mm. has been observed. The known electric wave spectrum has thus been extended toward shorter waves by an interval of from two to three octaves.

THE OPTICAL CONSTANTS OF CERTAIN LIQUIDS FOR SHORT ELECTRIC WAVES.

By J. D. Tear.

[ABSTRACT.]

IN crossing the hitherto unexplored region of the spectrum extending from the extreme infra-red to the shortest electric waves, the reflection and absorption coefficients and the indices of refraction of a number of liquids undergo unusual changes. A notable example is water which for $\lambda 0.3$ mm. has an index near that for the visible region of the spectrum, but for $\lambda 30$ mm. has a refractive index of 8.5, which is very nearly that for an infinite wave-length, *i.e.,* the square root of the dielectric constant. Experiments, described in the preceding abstract,[1] are now in progress which, it is hoped, will ultimately make a more complete exploration of this region possible. With the present equipment and methods the optical constants of a number of liquids, *i.e.,* water, glycerin, methyl and ethyl alcohol for the wave-lengths 4, 8, 11, 18, and 27 mm., have been determined.

The refractive indices have been computed by the Cauchy-Quincke formula from measured values of the coefficients of reflection and absorption. A second approximate, though direct determination of the refractive index, has been obtained by measuring the combined reflection from both surfaces of a thin liquid layer floated on mercury. As the thickness of the layer is varied, interference effects cause the reflected energy to pass through a series of maxima and minima which give a direct measurement of the wave-length in the liquid which divided into the wave-length in air gives the refractive index. The results obtained by these two methods are in good agreement.

The Thermal Stresses in Solid and in Hollow Circular Cylinders Concentrically Heated. CHARLES H. LEES. (*Proc. Royal Soc.,* A 712).—" The large differences of temperature which exist between the inside and outside of the heating or firing tunnels used in pottery and other works, and between the inner and outer portions of the concrete or masonry pillars supporting the floors of a building in which a fire occurs, make the thermal stresses approach the breaking strength of the materials and they are crushed or torn asunder." These stresses have hitherto been calculated only under the assumption of certain limiting simplifications. The author solves the problem in a more general way and shows "that for any temperature distribution, with any law of expansion, the stresses may be found by a simple graphical method so long as the variation of the elastic constants with the temperature may be neglected."

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[1] E. F. Nichols and J. D. Tear, " Short Elecrtic Waves."

After the problem has been solved the solution is applied to definite cases occurring in industry such as the putting out of service of a pottery kiln. "The sudden cooling of the interior of a furnace such as that described above will therefore subject the interior of the wall to tensile stresses in both longitudinal and tangential directions much above the tensile strength of the material, and radial cracks will be produced at the inner surface, which, since the stresses are equal in the two directions, will run indiscriminately longitudinally and tangentially. Through the kindness of Sir Robert Hadfield I have been able to inspect the walls of furnaces which have been in use for various periods at the Hecla Works, Sheffield, and I find that the above results are confirmed by experience." An explanation is furnished also of the cracks which exist within columns that have been subjected to fire and which do not show themselves at the surface.

This paper will in the future be used in the design of structures.

G. F. S.

The Dielectric Constant of Mica. J. R. WEEKS, JR. (*Phys. Rev.*, April, 1922).—Eighteen samples of mica of twelve different grades were measured. For sheets without visible air films the value of the constant was found to range from 6.4 to 9.3. Sheets having included air films seemed to give values from 2.9 to 5.6. Thin sheets split from the sample which had given 2.9 were measured and the results varied from 6.6 to 8.4. Other similar experiments confirm the belief that the low results are to be attributed to the presence of air. Thus is probably explained the wide divergence between values of the dielectric constant of mica given in handbooks.

G. F. S.

The Departure from Ohm's Law in Gold and Silver at High Current Densities. P. W. BRIDGMAN. (*Phys. Rev.*, April, 1922).—A method has been devised of attaining current densities of 5,000,000 amperes per sq. cm. along with the possibility of correcting the resistance for the increase of temperature. With these high current densities the resistance was found to increase about 1 per cent., the proportional increase being larger in thick than in thin gold and also greater for gold than for silver.

G. F. S.

NOTES FROM THE RESEARCH LABORATORY, EASTMAN KODAK COMPANY.*

THE 6-ALKYLOXYQUINALDINES.[1]

By H. LeB. Gray and G. O. Gutekunst.

[ABSTRACT.]

THE preparation of the 6-alkyloxyquinaldines involved the preparation of relatively large quantities of the paraminophenyl alkyl ether either by (1) preparation of the paranitrophenyl alkyl ether and reduction to the amino compound or (2) preparation of the paraceto-aminophenyl alkyl ether and hydrolysis by means of sulfuric acid. Several of the paranitrophenyl alkyl ethers had been previously prepared by heating for six hours the potassium salt of paranitrophenol in 16 per cent. alcoholic solution with the desired alkyl bromide or iodide in an autoclave at 170°–180° C. These ethers were prepared by boiling under a reflux for twelve hours a solution of the potassium salt of paranitrophenol in aqueous alcohol and the desired alkyl bromide or iodide. In a few cases the addition of the corresponding alcohol was necessary. The aceto-aminophenyl alkyl ethers were prepared in the same way, starting with paraceto-aminophenol. The following undescribed compounds were prepared: Paranitrophenyl butyl ether, fine white needles from alcohol, M. P. 32°; paraminophenyl butyl ether, light yellow oil boiling at 143°–144° at 12 mm.; paranitrophenyl iso-amyl ether, pale yellow oil boiling at 183° at 18 mm.; paraminophenyl iso-amyl ether, pale yellow oil boiling at 149°–150° at 15 mm.; paraceto-aminophenyl allyl ether, minute crystals from benzol, M. P. 88°–89°; paraminophenyl allyl ether, light yellow oil boiling at 143°–144° at 13 mm.; paraceto-amino phenyl butyl ether, white needles from benzol, M. P. 112°; paraceto-aminophenol benzyl ether, white needles, M. P. 142°; paraceto-aminophenyl iso-butyl ether, white needles, M. P. 80°–81°; paraminophenyl iso-butyl ether, colorless oil boiling at 145°–146°, at 10 mm.; paraceto-aminophenyl iso-amyl ether, white plates

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* Communicated by the Director.

[1] Communication No. 138 from the Research Laboratory of the Eastman Kodak Company and published in *J. Amer. Chem. Soc.*, August, 1922, p. 1741.

from benzol, M. P. 102°–103.5°; (the quinaldines were prepared by the Doebner-Miller quinaldine synthesis) 6-propyloxyquinaldine, light yellow liquid boiling at 176°–177° at 16 mm.; 6-propyloxyquinaldine ethiodide, pale yellow needles from ether alcohol, M. P. 147.5°; 6-allyl oxyquinaldines, red oily liquid; 6-allyl oxyquinaldine ethiodide, small yellow needles from ether alcohol; 6-butyl oxyquinaldine, yellow needles from petroleum ether, soften at 48° and melt at 52°; 6-butyl oxyquinaldine ethiodide, yellow needles from ether alcohol, M. P. 186°; 6-iso-butyl oxyquinaldine, colorless oily liquid boiling at 171°–172° at 12 mm.; 6-iso-butyl oxyquinaldine ethiodide, yellow needles from ether alcohol, M. P. 142°; 6-iso-amyl oxyquinaldine, light yellow liquid boiling at 182°–183°, at 10 mm.; 6-iso-amyl oxyquinaldine ethiodide, yellow needles from ether alcohol, M. P. 201°.

PRELIMINARY INVESTIGATIONS ON SILBERSTEIN'S QUANTUM THEORY OF PHOTOGRAPHIC EXPOSURE.

By A. P. H. Trivelli and L. Righter.

[ABSTRACT.]

THIS is a paper on the experimental investigation of the light quantum theory recently proposed by Doctor Silberstein.[3] The experiments were intended primarily for a study of the effect of clumping of silver halide grains in a photographic emulsion. It was found that clumps acted as single grains for development to the limit, thereby giving a very large range of grain sizes. These data afford a very rigorous test for Silberstein's theory which is essentially:

$$\frac{k}{N} = 1 - e^{-na}$$

where N is the original number per unit of the plate, of the class of size (area) a, n the number of incident light quanta, again per unit area of plate, and k the number of grains effected.

A brief description of the experimental procedure and table of results are given. The agreement of the observed results with those calculated from Silberstein's formula is very pronounced.

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[2] Communication No. 141 from the Research Laboratory of the Eastman Kodak Company and published in *Phil. Mag.*, July, 1922, p. 252.

[3] *Phil. Mag.*, 1922, p. 257.

NOTES FROM THE U. S. BUREAU OF CHEMISTRY.*

A METHOD FOR THE DETERMINATION OF AMINO NITROGEN AND AMMONIA IN CREAM AND BUTTER.[1]

By L. W. Ferris.

[ABSTRACT.]

In order to measure the relative proportion of amino nitrogen in milk, cream, buttermilk, and butter, it is desirable to have a procedure that is adaptable to all of these products. A method using picric and acetic acids, devised in the Bureau of Chemistry, has the following advantages:

1. Easy and rapid separation of the proteins and more complex substances from the lower degradation products, principally amino acids.
2. Hydrolysis of proteins during analysis is reduced to a minimum.
3. The filtrate can be held without further change, allowing a reasonable time between preparation of sample and analysis.
4. A correlation between amount of amino nitrogen and quality of sample.

By this procedure the amino nitrogen and ammonia in fourteen samples of fresh butter from sweet cream was found to range from 0.9 to 2.3, with an average of 1.4, expressed as percentage of the total nitrogen.

STUDIES ON THE DIGESTIBILITY OF PROTEINS IN VITRO. III. ON THE CHEMICAL NATURE OF THE NUTRITIONAL DEFICIENCIES OF ARACHIN.[2]

By D. Breese Jones and Henry C. Waterman.

[ABSTRACT.]

Estimations of the digestibility *in vitro* of variously treated preparations of arachin (the principal protein of the peanut, *Arachis hypogæa*) by the method of Waterman and Johns, indicate: (1) That this protein is incompletely digestible, and that

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* Communicated by the Chief of the Bureau.

[1] Published in *J. Dairy Sciences,* 5, July, 1922, 399.

[2] Published in *J. Biol. Chem.,* 50, June, 1922, 357.

this condition is not altered by boiling with water at ordinary pressure or by cooking under a steam pressure of fifteen pounds; and (2) that the nutritional failure of arachin is due to the retention of a considerable part of one or more of the essential amino acids, the most conspicuous of which is histidine, in the indigestible complex. The total amino acid composition of arachin would almost certainly be quite adequate, if it were available.

A direct comparison of the digestibility *in vitro* of arachin with that of casein and of cooked phaseolin gave the following (average) values for percentage of digested nitrogen, calculated on the basis of the total amino, *minus* free amino nitrogen: Arachin, 48.5; casein, 61.4; cooked phaseolin, 58.7. The control proteins are known to be sufficiently digestible to be available. An extremely indigestible partial cleavage product, produced by warming arachin with 0.1 N sodium hydroxid for two hours and precipitating the unattacked residue with very dilute acid, contained somewhat more than two-thirds of the total histidine, and about two-fifths of the total lysine of the arachin from which it was derived.

The experiments indicate that the incomplete digestibility of arachin is not due to changes brought about by the treatment involved in its isolation, but is a native property of the protein. The high nutritional efficiency of peanut meal is therefore to be attributed to the presence in the meal of sources of amino acids which supply essentials contained in an unavailable form in arachin.

THE PLAGIOCLASE FELDSPARS AS A CASE OF ATOMIC ISOMORPHISM.[1]

By Edgar T. Wherry.

[ABSTRACT.]

THE structural formula viewpoint is incapable of accounting for the isomorphism of the plagioclases, the arithmetical viewpoint mistakes a corollary for a cause, and only the atomic isomorphism viewpoint really corresponds to the data. As sodium is indicated by X-ray measurement to occupy approximately the same volume as calcium, and aluminium as silicon, the two feldspars may well have identical geometrical structures; the valence relations in solution merely require the one replacement to be accompanied by the other, and do not persist into the solid form of the compounds. Orthoclase and carnegieite can not be isomorphous with anorthite because the potassium atom of the one, and still more the two sodium atoms of the other, demand more space than displacement of the calcium can furnish. The simplest formulas adapted to bring out all the relations are: Albite, $NaAl(Si_3O_8)$; anorthite $CaAl(AlSi_2O_8)$.

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[1] Published in *Am. Mineralogist*, 7, July, 1922, 113.

Additions to Research Staff of the Eastman Kodak Company.—The following experts have recently been added to the laboratory of this company: Dr. Helge Schibsted, formerly with the Atmospheric Nitrogen Company; Clyde Brockett and D. H. Harris, Massachusetts Institute of Technology, 1922; A. Burgess, Bates College, 1922; R. P. Loveland, Grinnell College, 1922. H. L.

The Frequency-Sensitivity of Normal Ears. H. FLETCHER and R. L. WEGEL. (*Phys. Rev.*, June, 1922).—The sensitivity of the ear is here given in terms of the alternating (root mean square) pressure requisite for the production of a minimum audible sensation. "A tone of 1000 cycles per second requires only one-sixtieth as much pressure variation for audition as a tone at 100 cycles per second. The average sensitivity for normal ears varies from .15 dyne at 60 cycles to .001 dyne at 1000 cycles. Between 1000 and 4000 cycles the sensitivity is approximately constant and equal to .001 dyne per square cm."

An inspection of the curves connecting pitch and sensitivity in terms of pressure leads to the thought that individual differences are as sharply characteristic as they are in thumb prints. For instance, one person manifested a remarkable drop in sensitivity at 3000 cycles, and this held for both ears, though until 4500 cycles was reached the left ear exceeded its fellow in sensitivity. For the range of frequencies used in speech the following relations are stated: "Persons who have normal hearing require approximately .001 dyne per square centimetre in order to hear sounds in this range. Persons who require pressure variation of .1 dyne per square centimetre are called slightly deaf. Those who require one dyne are partially deaf but can usually follow ordinary conversation. Those who require 10 dynes belong to that class who use ear trumpets or deaf sets to amplify the speech waves. A pressure variation of approximately 1000 dynes can be felt and produces a sensation of pain.

"This shows that among people who can follow ordinary conversation there is a range in ear sensitivity of more than 1000 and among people who are noticeably deaf there is another range of 1000, making a total range of more than a million for people who can hear or be made to hear by means of amplifying devices." G. F. S.

Manufacture of Carbon Disulphide in the Electric Furnace.—George A. Richter of the Research Department of Brown and Company, Berlin, N. H., contributed to the forty-second general meeting of the American Electrochemical Society a paper embodying the results of experiments on the production of carbon disulphide by the Taylor process, although differing somewhat from the original form of that process. Large-scale production of the substances is based upon the direct action of the two elements at a temperature ranging from 600 to 1000° C., at which temperature the sulphur is, of course, in the form of vapor and the carbon an incandescent solid. Not all forms of carbon are admissible; anthracite, gas coke and other dense forms cannot be used. Good grades of willow or birch charcoal are among the best, especially those with a low ash content. The materials should be as dry as practicable. Water vapor will form hydrogen sulphide and other sulphur compounds. The charcoal should be well burned. The mechanical arrangements are described in the article, and the thermal data are presented in much detail. The conclusions are that a comparatively recent process for the manufacture of carbon disulphide has been devised and actual plant data indicate that the unit operates with reasonably fair thermal efficiency.

H. L.

Magnetostriction with Small Magnetizing Fields. J. R. HOBBIE, JR. (*Phys. Rev.*, May, 1922).—Joule as long ago as 1847 studied the change in length of a piece of iron upon the application of magnetic forces. Later Bidwell found that iron grew longer until a certain magnetizing force was attained. After this point it shortened. Nickel, on the other hand, contracted from the first application of force and no magnetizing field caused it to do anything but contract.

This investigation is limited to a study of magnetostriction with small fields. No new results came to light that are of a striking character. The importance of the work lies in this. Previous investigators in this field have been able to detect a change of length of one part in one hundred million while here three parts in a billion billion can be noticed. The sensitiveness has been made three thousand fold as great.

The piezo-electric properties of quartz and of Rochelle salt were made use of. The wire under examination hung from the crystal and was magnetized by a coil carrying an alternating current. The alternating magnetic field set up periodic changes in the length of the wire and the crystal was subjected to corresponding changes of tension, which, in turn, produced an alternating electromotive force between its tinfoil coatings. From a study of this it was possible to infer the extent of the changes of length of the wire. The method has the weakness that it does not discriminate between an elongation and a contraction due to the field.

A careful search was made for electrostriction in bismuth, but no trace of it was found.

G. F. S.

NOTES FROM THE U. S. BUREAU OF MINES.*

EXPERIMENTAL PRODUCTION OF ALLOY STEELS.

By H. W. Gillett and E. L. Mack.

The Bureau of Mines has prepared a number of series of alloy steels for the Army and Navy, the Vanadium Corporation, and the Welsbach Company, containing such alloying elements as uranium, vanadium, tungsten, molybdenum, cerium, boron, and zirconium, alone and in various complex alloys. The steels prepared were studied with reference to the alloy recovery, the character and composition of the ingot, and their metallurgical behavior in the furnace. The Bureau of Standards and a number of commercial steel companies have coöperated in this work.

Some of the conclusions derived from this work are as follows:

The use of a small direct arc furnace for making small experimental heats of alloy steel is attended with difficulty because of the carbon content. Indirect arc types allow much better control of the carbon.

Since the composition of many of the steels prepared is suitable only for special use, no direct conclusions can be drawn as to the value or lack of value of zirconium, titanium, uranium, boron, and cerium as true alloying elements in commonly used types of steels. The results of the physical tests so far have not in general been promising.

Even in very small ingots of 50 to 100 pounds, notable segregation of uranium, zirconium, or cerium generally appears when over about one-half per cent. of the first, or about one-third per cent. of either of the two latter is present in the steel.

These readily oxidizable elements are best added in the ladle, or to the furnace immediately before pouring. In remelting scrap containing these elements, they will be almost wholly lost, even in electric-furnace melting.

Uranium, and especially zirconium alloys used to introduce these elements into steel, should apparently be as free from carbon as possible. Alloys of zirconium with silicon or nickel, or both, give fair recoveries of zirconium, but no ferrozirconium tried does.

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* Communicated by the Director.

Titanium does not segregate as readily as zirconium, and its recovery from the ferro is higher; but in large amounts it is likely to segregate, and its recovery is not usually quantitative, although it may be quantitative if it is protected by the presence of a more readily oxidizable element, such as zirconium.

Although these elements are readily oxidized, none of them appears to be as efficient as aluminum or vanadium in degasifying "wild" steel. No special study has been made of very small amounts of these elements used as scavengers only, but all seem likely to leave their oxides or other compounds trapped in the steel as inclusions when added immediately before pouring, as is necessary in order to get a good recovery when using them as alloying elements rather than as scavengers.

Boron is almost quantitatively recovered when added at the end of the heat, and may be added at the start of the heat without great loss. In the amounts studied up to 0.6 per cent., no appreciable tendency to segregation was noted.

Further information on the tests will be found in Bulletin 199, recently issued by the Bureau of Mines.

INCLUSIONS IN ALUMINUM ALLOY SAND CASTINGS.

By Robert J. Anderson.

On account of the difficulty experienced by many aluminum-alloy foundrymen in eliminating hard spots from aluminum alloys, with resulting trouble in machining the casting, the Bureau of Mines made a study of inclusions in castings, with a view to putting the available knowledge of different operators on record and suggesting preventive methods.

The results indicate that the losses from hard spots are sufficiently serious to require the careful attention of all foundries, but the experience of many of the foundries has shown that close attention to certain aspects of foundry practice may substantially prevent their occurrence, particularly in preventing foreign materials, such as dirt, pieces of crucibles, etc., from being charged with the floor cleanings and scrap.

The results are more fully described in Technical Paper 290 of the Bureau of Mines.

CORROSION UNDER OIL FILMS, WITH SPECIAL REFERENCE TO THE CAUSE AND PREVENTION OF THE AFTER-CORROSION OF FIREARMS.

By **Wilbert J. Huff.**

Toward the end of the World War, the Bureau of Mines was requested to investigate the causes of after-corrosion upon the bore surfaces of the infantry service rifles, with the ultimate purpose of developing some simple procedure for eliminating this serious menace. The Bureau was especially fitted for conducting such an investigation because of its previous work on the preservation and utilization of our metal resources, and because of the experience of certain of its members in explosives and oils. Experiments had hardly begun when the Armistice was signed, but as the problem is important because of its applications both in war and in peace, continuance of work on it was deemed advisable. The Ordnance Department of the Army says that probably more rifles are ruined by improper preparation for storage than by any other cause; and the problem, though primarily military, touches the interest of every owner of a firearm.

The importance of this study is not, however, limited to the users of firearms. The fundamental problem proved to be corrosion under oil films; this differentiates after-corrosion sharply from the ordinary corrosion of clean iron and steel surfaces. It was found that this after-corrosion is closely allied to a number of other general problems, such as the corrosion under oil of bright steel parts after handling in manufacturing operations, and to the corrosion under oil experienced near the ocean.

A critical laboratory study, comprising the exposure of fired rifles and fouled barrel sections to known humidities, the chemical examination of the corrosive residue, the use of special ammunition, and the analysis and testing of many " nitrosolvents " and other compositions recommended as preventives showed:

The present high-pressure smokeless cartridge leaves no nitrocellulose residue and no corrosive acid residue. After-corrosion following the use of such cartridges is caused by (1) the explosive deposition of a water-soluble salt or salts in whose aqueous solution the steel corrodes, together with subsequent exposure to (2) a high humidity and (3) the presence of oxygen. In the present service ammunition this salt is potassium chloride from the decomposition of the chlorate in the primer.

Such water-soluble salt or salts are retained in tool wounds and pits on the bore surfaces, in which they can not be seen and from which they can not be removed mechanically. They are easily dissolved by water or suitable aqueous solutions.

After-corrosion may also be prevented by keeping both ends of the bore tightly corked.

The present service ammunition can be rendered non-corrosive by eliminating the chlorate of the primer. It may be possible to develop a non-corrosive primer that will not affect the present ballistic properties of the cartridge. This point is under investigation.

A number of non-aqueous compositions recommended for cleaning firearms possess little or no value. Their supposed virtue seems to rest on tests conducted at humidities so low that no corrosion could occur.

After-corrosion proceeds below the dew point.

A simple test for differentiating between worthless and valuable cleaning compounds was devised.

Further information may be found in the report on the results of this work, published as Technical Paper 188 of the Bureau.

Prototypes of the International Ohm. Paul Janet. (*Comptes Rendus*, July 10, 1922.)—In the years following the conference held in Washington in 1910 for the consideration of the silver voltameter and for the fixing of the ampere, many of the national physical laboratories have constructed standard mercury ohms. Even before this René Benoît, who made the standard ohms for France in 1883, had announced his intention of resuming this type of work and of preparing 10 mercury standards. This he set about, not as his duty as the official head of the International Bureau of Weights and Measures, but as a scientific labor of love. After his tubes had been selected and calibrated they were transported to the Central Electrical Laboratory where a special apparatus for the distillation of mercury in vacuum had been installed. The process of filling them with the liquid in a vacuum had been completed and the ohm standards were ready for measurement when the war broke out. During the bombardment of Paris by the invaders these precious products were carefully protected. It was not till 1919 that work was resumed. Then it was deemed necessary to refill them. The eight tubes that have stood all tests have now been completely determined. On the average the divergence between the resistance calculated from their dimensions and the measured resistance amounts only to nineteen millionths. How much care, labor and scientific acumen have been needed to bring to a successful termination this long series of processes is known only to the metrologist. G. F. S.

THE FRANKLIN INSTITUTE.

(Proceedings of the Stated Meeting held Wednesday, October 18, 1922.)

Hall of The Franklin Institute,
Philadelphia, October 18, 1922.

Mr. W. C. L. Eglin, Vice-president of the Institute, *in the Chair.*

The Board of Managers submitted their report. The report recorded the elections to membership of:

Murray C. Boyer, Esq., Solicitor of Patents, 806 Franklin Trust Building, Philadelphia, Pennsylvania;

Roland L. Eaton, Esq., 20 South Eighteenth Street, Philadelphia, Pennsylvania;

Joseph F. Greene, Esq., B.S., Chemical Engineer, Kimble Glass Company, Vineland, New Jersey;

Robert Hatfield Irons, Esq., President, Central Iron and Steel Company, Harrisburg, Pennsylvania;

Ernest Edward Johnson, Esq., B.S., M.S., Professor of Physics, Northeast High School, Philadelphia, Pennsylvania;

William B. Leighninger, Esq., B.A., M.A., Teacher of Chemistry, Frankford High School, Philadelphia, Pennsylvania;

John E. Symons, Esq., Mechanical Engineer, The Texas Company, New York City, New York;

James A. Wright, Wright-Fisher Engineering Company, Detroit, Michigan;

a lecture before Sections by

Herbert E. Ives, Ph.D.,
Research Laboratories,
The American Telephone and Telegraph Company and Western Electric Company, Incorporated, New York City, New York,

on "The Primary Standard of Light";

and additions to the library by gift, 322 volumes and 356 pamphlets; by purchase, 68 volumes and 1 pamphlet and by binding, 272 volumes.

The Board of Managers also transmitted the following preambles and resolution prepared by a special committee appointed by them to consider, at the request of the Board of Trustees, the advisability of certain changes in the By-Laws:

> Whereas, doubt has arisen as to the meaning of the following provisions of Section 1 and Section 6 of Article 1 of the By-Laws, namely, the words "In the way and manner hereinafter provided so that the same shall not in any event be liable for the debts of the Institute," after the word "Institute" (Section 1), and the last paragraph of Section 6 as follows: "The principal and interest of all trust funds shall not be liable for debts of the Institute but shall be devoted to

> its continuance and preservation," and counsel having advised that in their opinion the principal and income from the unlimited trust estates may be applied by the Board of Trustees to the current expenses and obligations, or other legal purposes of the Institute, but advise that the By-Laws should be amended so that all doubt with respect to such power should be removed,
>
> AND WHEREAS, so that the purposes of the use of these trust funds as affected by the By-Laws may be clear of doubt;
>
> *Resolved*, that the words "in the way and manner hereinafter provided so that the same shall not in any event be liable for the debts of the Institute," in Section 1 of Article 1 be omitted and stricken therefrom, and that the last paragraph of Section 6 of Article 1, as follows: "The principal and interest of all trust funds shall not be liable for debts of the Institute but shall be devoted to its continuance and preservation," be omitted and stricken therefrom, and that Section 1 of Article 1 and Section 6 of Article 1 be amended so as to read as now expressed with the omission of the said words,

and recommended to the Institute their adoption.

Doctor Hoadley moved that the recommendations of the Board of Managers as to amendments to Sections 1 and 6 of the By-Laws of the Institute be voted on at the next Stated Meeting in accordance with Article 17, By-Laws of the Institute. This was duly seconded and unanimously carried.

The Board further reported that at their meeting held on the afternoon of Wednesday, September 13, 1922, Mr. W. C. L. Eglin was elected Vice-president of the Institute to serve until the next regular election of officers in January. It was explained that the need for this action was occasioned by the absence of Dr. Walton Clark, President, and the death of Mr. Coleman Sellers, Jr., Vice-president; also it was pointed out that while the By-Laws embody no specific provision for the election of a Vice-president before the annual meeting of the Institute, the Institute's attorneys, Messrs. Brown and Williams, advised that presumably the power to fill a vacancy is vested in the Board of Managers, subject to ratification by the Institute. The matter of confirming this election was then presented to the Institute for action.

On motion of Doctor Alleman, seconded by Doctor Keller, the election of Mr. W. C. L. Eglin as Vice-president of the Institute by the Board of Managers was confirmed.

A report of progress was presented by the Committee on Science and the Arts.

The Chairman then announced that the next business of the meeting would be the presentation of the Howard N. Potts Medal jointly to John M. Weiss, Esq., B.S., and Charles Raymond Downs, Esq., Ph.D., for "their notable achievement in the scientific and commercial development of the catalytic vapour-phase oxidation of benzene to maleic acid and their pioneer work in developing a commercial process for changing aromatic to aliphatic compounds" and recognized Dr. H. J. M. Creighton of the Committee on Science and the Arts.

Doctor Creighton said, "*Mr. President:* After careful and thorough investigation, the Institute's Committee on Science and the Arts recently recommended the award of the Howard N. Potts gold medal jointly to Messrs.

John Morris Weiss and Charles Raymond Downs, for their notable achievement in the scientific and commercial development of the catalytic, vapour-phase oxidation of benzene to maleic acid, and for their pioneer work in the development of a commercial process for changing aromatic to aliphatic compounds. This medal, as you know, Sir, is awarded by the Institute for important development of previous basic discoveries, and for inventions or products of superior excellence or utilizing important principles. In the opinion of the Committee on Science and the Arts, the process invented by Messrs. Weiss and Downs more than fulfils the requirements for the award of this medal.

"In the principle, the process is simple, and consists in passing a predetermined mixture of benzene vapour and air over a heated catalyst, by the aid of which the benzene nucleus is split and changed to maleic anhydride which is subsequently converted into maleic acid by absorption in water. In reality, the catalytic, vapour-phase oxidation presents many difficulties, owing to the large number of factors affecting the reaction. These difficulties have been overcome successfully by Messrs. Weiss and Downs.

"Formerly, maleic acid was a laboratory curiosity costing five dollars an ounce; now, it is manufactured by the Weiss and Downs process in large quantities at a low price. Most of this acid is transformed to malic acid, a food product which is used to replace the more expensive citric acid; but, when the low cost and very reactive nature of maleic acid are considered, there is opened up for the future the possibility of numerous, pure organic syntheses, and the commercial production of many straight chain acids hitherto obtainable only from expensive natural sources.

"I have the honour to present to you, Sir, Mr. Weiss, joint inventor of the catalytic process for the vapour-phase oxidation of benzene, who has come here this evening to receive the Howard N. Potts gold medal on behalf of Doctor Downs and himself."

The Chairman then presented the medals and accompanying documents to Mr. Weiss, who thanked the Institute for the high honor conferred upon him and his associate.

The Chairman then introduced Dr. Arthur L. Day, Director of the Geophysical Laboratory, Carnegie Institution of Washington, who presented the paper of the evening on "The Study of Earth Movements in California."

The speaker pointed out that there appears to be a better opportunity for the study of earth movements in considerable variety in California than in any other locality, except Japan. It is a region of complex geologic structure and great difference of elevation (loading) resulting in gravitation anomalies and land slips of considerable magnitude. It is proposed to study these (1) through astronomical observations of latitude for the detection of crustal creep, (2) through accurate triangulation and precise levels for the determination of local surface movements, (3) through special seisometric apparatus now building for the determination of sub-surface movement, including the place of origin of earthquake tremors, their direction of propagation and magnitude with reference to the existing faulting, (4) the location of major fault scarps off the coast which may contribute to these movements. The investigations which will cover a period of years will be conducted by the Geophysical Laboratory, the United States Geological Survey and the United States Coast and Geodetic Survey.

After brief discussion, a rising vote of thanks was extended to the speaker.

Adjourned.

R. B. OWENS,
Secretary.

COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of Stated Meeting held Wednesday, October 4, 1922.)

HALL OF THE INSTITUTE,
PHILADELPHIA, October 4, 1922.

DR. H. J. M. CREIGHTON *in the Chair.*

The following reports were presented for final action:

No. 2790: Automatic Cashier. The Edward Longstreth Medal to Mr. Edward J. Brandt of Watertown, Wisconsin.

No. 2796: Noiseless Typewriter. The Edward Longstreth Medal to The Noiseless Typewriter Company of New York.

R. B. OWENS,
Secretary.

MEMBERSHIP NOTES.

ELECTIONS OF MEMBERSHIP.

(Stated Meeting, Board of Managers, October 11, 1922.)

RESIDENT MEMBERS.

MR. WILLIAM N. LEIGHNINGER, 1123 Harrison Street, Philadelphia, Pennsylvania.

NON-RESIDENT.

MR. JOSEPH F. GREENE, Kimble Glass Company, Vineland, New Jersey.

CHANGES OF ADDRESS.

MR. E. G. BASHORE, The Texas Company, Port Arthur, Texas.
MR. HERBERT S. BERLINER, Compo Company, Ltd., 131–18th Avenue, Lachine, Canada.
MR. GEORGE L. BOURNE, The Superheater Company, 17 East 42nd Street, New York City, New York.
MR. R. L. BRINTON, 3700 Kensington Avenue, Philadelphia, Pennsylvania.
MR. A. CHRISTIANSON, P.O. Box 877, Butler, Pennsylvania.
MR. CLARENCE E. CORNELIUS, 162 West Coulter Street, Germantown, Philadelphia, Pennsylvania.
MR. PATRICK B. DELANY, South Orange, New Jersey.
MR. FRANCIS X. DAILY, 109 St. Pauls Road, Ardmore, Pennsylvania.

Mr. Walstein F. Douthirt, 1752 Equitable Building, New York City, New York.
Mr. Rolfe E. Glover, Jr., 2435 West Eighteenth Street, Wilmington, Delaware.
Mr. William H. Harding, 1736 Land Title Building, Philadelphia, Pennsylvania.
Mr. Roy Linden Hill, Atlas Powder Company, Tamaqua, Pennsylvania.
Mr. E. E. Keller, Hotel Sagamore, Rochester, New York.
Mr. C. T. Mack, 1208 Decatur Street, N. W., Washington, D. C.
Mr. J. W. Walker, Devon, Pennsylvania.
Mr. Wm. R. Warner, Jr., "Sulgrave," Malvern P. O., Chester County, Pennsylvania.

NECROLOGY.

Mr. W. N. Best, 11 Broadway, New York City, New York.
Mr. Louis H. Eisenlohr, 932 Market Street, Philadelphia, Pennsylvania.
Mr. F. P. Howe, 242 South 17th Street, Philadelphia, Pennsylvania.
Mr. Henry D. Justi, 32nd and Spring Garden Streets, Philadelphia, Pennsylvania.
Mr. A. Robinson McIlvaine, Fifteenth and Hamilton Streets, Philadelphia, Pennsylvania.
Mr. Emerson McMillin, Darlington Farms, Mahwah, New Jersey.
Mr. R. Quayle, 233 N. Harvey Avenue, Oak Park, Illinois.
Mr. John Rae, 4945 Larchwood Avenue, Philadelphia, Pennsylvania.
Dr. Jokichi Takamine, Equitable Building, New York City, New York.

LIBRARY NOTES.

PURCHASES.

Advisory Committee for Aeronautics.—Technical Report for the Year 1911–12.
American Pharmaceutical Association.—Year Book, Volume 9, 1920. 1922.
American Society of Heating and Ventilating Engineers.—Transactions. 1920.
Annuaire Sucrier, 1921–22. 1922.
Bragg, Sir William.—Electrons and Ether Waves. 1921.
Ceramic Society.—Transactions, Collective Index of Volumes 1–20. 1921.
Chemical Engineering Catalogue, Ed. 7. 1922.
Glazebrook, Sir Richard.—Dictionary of Applied Physics, Vols. 1 and 2. 1922.
Gunther, R. T.—Early Science in Oxford, Part 2-Mathematics. 1922.
Kempf, Richard.—Tabellen der wichtigsten organischen Verbindungen. 1913.
Rolph, George M.—Something about Sugar. 1917.
Ullmann, Fritz.—Enzyklopädie der technischen Chemie, Vol. 11. 1922.

GIFTS.

Academia Nacional de Ciencias, Transactions. Cordoba, Republica Argentina, 1922. (From the Academy.)
Alabama Geological Survey, Bulletins 23, 24 and 25. University, Alabama, 1921. (From the State Geologist.)

Alpha Portland Cement Company, Alpha Aids. Easton, Pennsylvania, no date. (From the Company.)

American Institute of Mining and Metallurgical Engineers, Transactions, Vol. lxvii. New York City, New York, 1922. (From the Institute.)

American Society for Testing Materials, Year Book, August, 1922. Philadelphia, Pennsylvania, 1922. (From the Society.)

American Wood-Preservers' Association, Proceedings of the Eighteenth Annual Meeting. Chicago, Illinois, 1922. (From the Association.)

Anderson-Grice Company, Limited, Pamphlet on Stone Working Machinery. Carnoustie, Scotland, 1922. (From the Company.)

Armstrong Manufacturing Company, Catalogue No. 17. Bridgeport, Connecticut, 1922. (From the Company.)

Arrow Electric Company, Chained Lightning. Hartford, Connecticut, 1922. (From the Company.)

Barrett Company, Flotation Oils and Reagents. Philadelphia, Pennsylvania, 1922. (From the Company.)

Barrett, Haentjens and Company, Pamphlet on Centrifugal Pumps. Hazleton, Pennsylvania, no date. (From the Company.)

Beaumont, R. H., Company, Catalogue No. 52 on Skip Hoists. Philadelphia, Pennsylvania, 1922. (From the Company.)

Bibliotheca Universitatis Liberæ Polonæ, Jonston i de Spinoza, Probleme de Fourier pour le milieu rayonnant, Les proprietes du noyau resolvant de l'equation integrale d'un probleme aux limites. Varsaviæ, Poland, 1922. (From the Library.)

Birdsboro Steel Foundry and Machine Company, The Jackson Belt Lacer. Birdsboro, Pennsylvania, 1922. (From the Company.)

British Scientific Instrument Research Association, Durability of Optical Glasses. London, England, 1921. (From the Association.)

California Mining Bureau, Bulletins 2, 5, 20, 23, 24, 32, 36, 37, 38, 44, 45, 50, 53, 60, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 82, 83, 84, 86, 87, 88, 89, 90, Mining in California, Vol. 18, Nos. 1-5, Preliminary reports, Nos. 1-8 and Reports, xiv, xv, xvi, and xvii. San Francisco and Sacramento, California, 1903 to 1921. (From the State Librarian.)

Chapin-Skelton Corporation, Catalogue of Reamers, Boring-Bars, Lath Arbors, Counterbores, Production Tools, Special Machines. Syracuse, New York, 1922. (From the Corporation.)

Cleworth, Wheal and Company, Limited, The Wet and Dry Bulb Thermometer, Water Coolers, Air Filters and Natural Humidifiers. Castleton, Lancashire, England, 1922. (From the Company.)

Cochrane, H. S. B. W., Corporation, Cochrane Combined Catalogue. Philadelphia, Pennsylvania, 1922. (From the Corporation.)

College of Physicians of Philadelphia, Transactions, Vol. 43. Philadelphia, Pennsylvania, 1921. (From the College.)

Columbia University, Catalogue 1921-1922. New York City, New York, 1921. (From the University.)

Connersville Blower Company, Bulletin 21, Victor Pressure Blowers. New York City, New York, 1922. (From the Company.)

Copper and Brass Research Association, Copper—the Ideal Roof. New York City, New York, no date. (From the Association.)

Coventry Chain Company, Limited, Coventry Chains. Coventry, England, 1922. (From the Company.)

Crane Packing Company, Metallic Packing. Chicago, Illinois, 1922. (From the Company.)

Dansk Ingeniorforening, Aarbog for 1922. Kobenhavn, Denmark, 1922. (From the Society.)

Electric Power Club, Hand-book, 1922. St. Louis, Missouri, 1922. (From the Club.)

Electrical Alloy Company, Catalogue No. 10, Bulletins 1 to 10, inclusive, of Wire, and Copper. Morristown, New Jersey, no date. (From the Company.)

Elvin Mechanical Stoker Company, Bulletin 101, Elvin Mechanical Stokers. New York City, New York, 1922. (From the Company.)

Emerson Electric Manufacturing Company, Bulletins 3156 and 3180. St. Louis, Missouri, 1922. (From the Company.)

Finland Statistique Officielle, Sosialisia Erikoistutkimuksia, No. 1, 1917 and 1918, and No. 2, 1919, Statistique Ouvriere B, 1918 and 1919. Helsinki, Finland, 1921. (From the Bureau of Statistics.)

Firth-Sterling Steel Company, Blue Chip High-speed Steel. McKeesport, Pennsylvania, 1920. (From the Company.)

Fitzgibbons Boiler Company, Incorporated, The Fitzgibbons Boiler. New York City, New York, 1922. (From the Company.)

Grinnell Company, Bulletin, Industrial Piping. Providence, Rhode Island, 1922. (From the Company.)

Holst, K., and Company, Booklet on Ferro Concrete. London, England, 1922. (From the Company.)

Huntley Manufacturing Company, Catalogue No. 60, Grain Cleaners and Special Mill Machinery and Monitor Price Book. Silver Creek, New York, 1922. (From the Company.)

India Geological Survey, Memoir No. 2, Devonian Fossils from Chitral and the Pamirs by F. R. Cowper Reed. Calcutta, India, 1922. (From the Director.)

Instituto Geologico de Mexico, Boletin Num. 37. Mexico, Mexico, 1920. (From the Institute.)

Iron and Steel Institute, Journal, Vol. cv, No. 1, 1922. London, England, 1922. (From the Institute.)

Jewell Electrical Instrument Company, Catalogue No. 14. Chicago, Illinois, 1922. (From the Company.)

Johns-Pratt Company, Catalogue No. 100. Hartford, Connecticut, 1921. (From the Company.)

Jones, W. A., Foundry and Machine Company, Jones Gears. Chicago, Illinois, 1922. (From the Company.)

Kobert Machine Company, Inc., How Electric Riveting was Made Commercial. New York City, New York, 1922. (From the Company.)

Lackawanna Steel Company, Hand-book Containing General Information for the Use of Engineers, Architects and Builders. Lackawanna, New York, 1915. (From Mr. John J. L. Houston.)

Lipe, W. C., Lipe Automatic Gear Tooth Chamfering Machines. Syracuse, New York, no date. (From Mr. Lipe.)

Massachusetts State Department of Health, Report of Division of Food and Drugs for the Year Ending November 30, 1920. Boston, Massachusetts, 1921. (From the Department.)

Mohr, John, and Sons, Burton Duplex Water-tube Boiler. Chicago, Illinois, no date. (From the Company.)

Moore and Moore, Incorporated, Catalogue No. 10 on Drills and Reamers. Reading, Pennsylvania, 1922. (From the Company.)

Murphy and Son, Limited, Bulletin No. 6, Bureau of Bio-technology. London, England, 1922. (From the Company.)

New Zealand Department of Mines, Alphabetical List of New Zealand Tertiary Mollusca by Henry Sutor and Paleontological Bulletin No. 9, The Upper Cretaceous Gastropods of New Zealand. Wellington, New Zealand, 1922. (From the Department.)

Newton Engineering Department, Annual Reports of the City Engineers for 1920 and 1921. Newton, Massassachusetts. (From the Department.)

Northwestern Expanded Metal Company, Designing Data for Reinforced Concrete. Chicago, Illinois, 1922. (From the Company.)

Paragon Machine Company, Paragon Blue Printing Equipment. Rochester, New York, no date. (From the Company.)

Penn Iron and Steel Company, Booklet on Iron. Creighton, Pennsylvania, 1922. (From the Company.)

Pennsylvania Bureau of Topographic and Geological Survey, Bulletins 48, 49, 50, 51, 52, 53, and 56. Harrisburg, Pennsylvania, 1922. (From the Bureau.)

Pennsylvania Department of Labor and Industry, Proceedings of the Industrial Relations Conference. Harrisburg, Pennsylvania, 1922. (From the Department.)

Pennsylvania Pump and Compressor Company, Pamphlet No. 202, Centrifugal Pumps. Easton, Pennsylvania, 1922. (From the Company.)

Philadelphia Maritime Exchange, Forty-seventh Annual Report. Philadelphia, Pennsylvania, 1922. (From the Exchange.)

Philadelphia School of Design for Women, Booklet, Training for the Useful and the Beautiful. Philadelphia, Pennsylvania, 1922. (From the School.)

Phinny Brothers Company, The Importance of Correct Lubrication. Oil City, Pennsylvania, 1922. (From the Company.)

Purdue University, Bulletin, The Production of Nitric Oxides and Ozone by High Voltage Electric Discharge. Lafayette, Indiana, 1922. (From the University.)

Railway and Industrial Engineering Company, Transmission Switching and Protective Equipment. Greensburg, Pennsylvania, 1922. (From the Company.)

Reeves Pulley Company, Catalogue P-33. Columbus, Indiana, 1922. (From the Company.)

Reliance Gauge Column Company, Reliance Steam Specialities. Cleveland, Ohio, 1922. (From the Company.)

Safety Car Heating and Lighting Company, The Safety Fan. Philadelphia, Pennsylvania, 1922. (From the Company.)

St. Joseph's College, Catalogue 1921-1922. Philadelphia, Pennsylvania, 1921. (From the College.)

Serck Radiators, Limited, Booklet of Serck Radiators, Oil Coolers, Brass and Copper Tubes. London, England, no date. (From the Company.)

Soper, H. E., Frequency Arrays. Cambridge, England, 1922. (From the Author.)

Southern Pine Association, A Manual of Standard Wood Construction of Southern Yellow Pine. New Orleans, Louisiana, 1918. (From Mr. John J. L. Houston.)

Tagliabue, C. J., Manufacturing Company, Looking Into It. Brooklyn, New York, no date. (From the Company.)

Tasmania Department of Mines, Report of the Acting Secretary for Year Ending December 31, 1921. Hobart, Tasmania, 1922. (From the Department.)

United States Air Service, Information Circulars Nos. 346 and 352. Washington, District of Columbia, 1922. (From the Chief of Air Service.)

United States Department of Commerce, Fourteenth Census of the United States taken in the Year 1920, Vol. vi, Parts I and II, Agriculture. Washington, District of Columbia, 1922. (From the Department.)

University of Utah, Catalogue 1922-1923. Salt Lake City, Utah, 1922. (From the University.)

Van Keuren Company, Catalogue No. 25 of Measuring Tools. Boston, Massachusetts, no date. (From the Company.)

Western Tool and Manufacturing Company, Catalogue No. 19. Springfield, Ohio, 1922. (From the Company.)

Wilcox, Delos F., Solving the Traction Problem, What Shall We Do with the Street Railways? Service at Cost in Local Transaction, and Report on the Transit Problems for Bethlehem, Pennsylvania and Vicinity. Bethlehem, Pennsylvania, 1919. (From the Author.)

Williams Gauge Company, Bulletins B and C-2, Catalogue A-2 and Pamphlet on Gauges. Pittsburgh, Pennsylvania, 1922. (From the Company.)

Yellow Pine Manufacturers' Association, A Manual of Standard Wood Construction of Yellow Pine. St. Louis, Missouri, 1913. (From Mr. John J. L. Houston.)

CORRESPONDENCE.

LAFAYETTE, INDIANA, Sept. 22, 1922.

TO THE EDITOR,
JOURNAL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, PENNSYLVANIA.

DEAR SIR:

In my article on "Commutation in Continous Current Dynamos," published in the JOURNAL OF THE FRANKLIN INSTITUTE of May, 1922, reference is made to Mr. B. G. Lamme as being "the first to put the theory of commutation in a new light...." having in mind Mr. Lamme's method of considering the cutting of the various component fluxes by the conductors during commutation, and the avoidance of the usual expressions involving the coefficients of self and mutual induction. More than this is, however, included in the theory as presented in the article, and I feel that, since many other engineers have done valuable work in elucidating the difficult problems of commutation, additional names might have been mentioned in the introductory paragraphs. This would, however, have involved considerable research and care in order to avoid mistakes and the possibility of offending those whose contributions might have been overlooked or referred to with insufficient emphasis. There appears to be no doubt that the work of M. Marius Latour may be referred to without reference to other noted investigators, because so long ago as 1901-1902 he maintained against considerable opposition that if the average e.m.f. generated in the armature coil during short-circuit is to be zero, the total resultant flux linking with the coil at the end of commutation must be the same in amount as at the beginning of commutation, and this is, in effect, the fundamental principle underlying the method which is followed in my article.

Very truly yours,
(Signed) A. STILL.

BOOK NOTICES.

LEFAX RADIO HANDBOOK, by Dr. J. H. Dellinger, Chief, and L. E. Whittemore, Alternate Chief, Radio Laboratory, U. S. Bureau of Standards, Washington, D. C. Chapters I to VI inclusive. 12mo leather binding. Philadelphia, Lefax, Incorporated, 1922.

By employing a loose-leaf binder, characteristic of the Lefax Service, the publishers have issued a handbook which may be kept continuously revised as improvements in radiophony warrant the publication of supplementary matter. For a subject yet in an inchoate state and which is undergoing urgent research, a handbook of this character is to be preferred for the early literature of the art that is evolving out of the furore that marked the advent of radiophony.

There is no longer doubt whether a serious art is in formation, or a fad is being exploited commercially. The results already obtained are so intimate with the public that radiophony will presently be as essential as telephony. Though the whole subject is beset with elements of great uncertainty and complexity, and great limitations of its possible use are already evident, there remains a demonstrated popular demand for this means of communication in addition to its remarkable technical applications.

Commercially the research and experimental resources of the electrical industry are being employed for the development of radiophony more extensively than they have ever been devoted to a distinct subject; and these technical efforts are being supplemented by experimental labors in collegiate and individual laboratories.

Coëxistent with this development, transmitting stations are not only fast multiplying in number, but many are becoming elaborately expensive in their installation, and pretentious in the programs they broadcast.

For the general public radio communication may always mean the radiophony which may be popularly employed, or short-wave communication at vocable frequency; while high-frequency radio may always be called wireless telegraphy. It is to be feared that the handbooks for radio instruction will even lessen this discrimination, rather than emphasize it, as the present work is called simply "Radio Handbook." Yet in the near future it is possible that impulse-radio may become perfected to the exclusion of high-frequency communication on a code.

The popular fad, which the recent practical advent of radiophony has produced, has already its roll of amateurs of large and increasing numbers, whose zeal causes them to plunge boldly into the most complex of the esoteric subjects of physics, where those learned in such matters proceed with caution and even trepidation.

The commercial advertising and propaganda of this subject by great and small manufacturers of its apparatus, far from clarifying the situation, is raucously increasing the scientific confusion. The catalogues of such supplies read like the old books of alchemy, and are reminders of the medical charlatanry of the Middle Ages. One stands aghast at the magniloquent and occult trade names under which simple apparatus are exploited. Advertising psychology has been practiced here with an unscrupulous hand; a subject too abstruse and complex for amateurs' manipulation is by these means vexed with needless obscuration.

In addition the public prints have instigated the amateur to purchase materials and collaborate these into a receiving set whose scheme of connections he may vary at his whim. Even attempts at transmission are recklessly encouraged. While in some instances this propaganda is permissible, the amateur generally should be warned not to attempt the construction or collaboration of a radio set, but purchase an approved outfit according to his means and choice. The influence of induction, and especially of capacity, is so subtle and baffling to control, that the most practiced experimenter must proceed here with difficulty and much uncertainty.

The literature of radiophony has multiplied with as vigorous fertility as the apparatus; inevitably much of it is poor, if not misleading. The demand for an adequate and authoritative handbook is only made more urgent through this insistence of the prints, and the "Radio Handbook," by Dellinger and Whittemore, is one of the few which may be followed with confidence by the layman or amateur. Though unpretentious in size, in its six chapters the authors have traversed the elementary principles of this form of radio communication in a manner that is generally clear, and almost non-mathematical.

There are a few obvious omissions in it which subsequent editions should supply. The layman wants at the very outset to know how electrical transmission occurs through space. In attempting to explain this the authors have been not only unnecessarily brief, but confusing and contradictory. Though the hypotheses of the mechanism of an electro-magnetic wave-system are wholly fictitious, it is necessary in such handbooks to present in an elementary way the generally accepted fiction of an electro-magnetic wave. It is worth while to attempt to formulate this out of its heterogeneous mathematical suppositions, and obtain a comprehensible graphical representation of a wave-system of this nature.

A similar attempt should be made, assisted by a proper graphic, to explain why the electric displacement element of the electro-magnetic wave can produce a cumulative effect on the convolutions of a coil antenna, while the generating lines of magnetic force cause a zero potential in the coil by the induction of opposing e.m.f.s. within it. This would afford at once an explanation for the end-on directive action of a coil antenna.

Evidently by an oversight the misleading statement is made in Chapter V that, "radio circuits consist of two elements, called capacity and inductance." The proper phrasing of this matter is essential and the error should be corrected promptly.

There is need at this juncture for a general term to designate such apparatus as is variously called a "chopper," modulator, or interrupter. Probably the term impulser would be more inclusive than any yet employed. Precisely an impulser would be an instrument to superpose upon the transmitting wave-train the impulses of audible, or vocable, frequency.

WILBUR M. STINE.

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS. Report No. 129. Aeronautic Instruments—V—Power Plant Instruments, by the Aeronautic Instruments Section, Bureau of Standards. 72 pages, illustrations, quarto. Washington, Government Printing Office, 1922.

Report No. 129 of the Committee in five parts, covers the general field of power plant instruments.

Part I gives a fairly complete discussion of all the various types of airplane tachometers studied at the Bureau of Standards. French, German, and American chronometric tachometers are described in detail; also several types of foreign and domestic centrifugal tachometers.

Part II describes in detail the apparatus and methods of testing airplane tachometers at the United States Bureau of Standards. Also, the average results of tests on many instruments of the chronometric, centrifugal, magnetic, and air viscosity type are given and are discussed.

Part III describes the principal types of distance reading thermometers for aircraft engines, including an explanation of the physical principles involved in the functioning of the instruments and the proper filling of the bulbs.

Part IV discusses briefly the use of air and oil pressure gages on aircraft, and describes the construction of various American, British, and German gages.

Part V discusses the principal gasoline depth gages now in use and gives a general summary of the advantages and disadvantages of each type. A brief description is also given of two typical flowmeters.

Report No. 141. Experimental Research on Air Propellers—V, by W. F. Durand and E. P. Lesley. Leland Stanford Junior University, California. 82 pages, illustrations, quarto. Washington, Government Printing Office, 1922.

In the previous reports on experimental research on air propellers, by W. F. Durand and E. P. Lesley, as contained in the National Advisory Committee for Aeronautics reports Nos. 14, 30, and 64, the investigations were made progressively and each without reference to results given in preceding reports and covering only information relating to forms perhaps adjacent in geometrical form and proportion. The present report is a review of the entire series of results of the preceding reports with a view of examining through graphical and other appropriate means the nature of the history of the characteristics of operation as related to the systematic variation in characteristics of forms, etc., through the entire series of such characteristics. In reviewing the results a check was made of doubtful points by repetition of tests, to remove inconsistencies where found, and generally to develop for the series of models represented by these tests a consistent set of results as judged by the relation of those for any one model to those for all models adjacent in geometrical form and proportion. The report presents the results of this general analysis and review of the previous series of experimental observations. There is also added a series of nomographic diagrams for the rapid graphical solution of the problems such as are considered in the report. The diagrams have been prepared for both metric and English units.

A SHORT HANDBOOK OF OIL ANALYSIS. By Augustus H. Gill, S.B., Ph.D., Massachusetts Institute of Technology. Revised 10th edition, 223 pages, 12mo. Philadelphia and London, J. B. Lippincott Company, 1922. Price $2.50.

The fact that ten editions of this work have been issued in a quarter of a century testifies sufficiently to its merits and accuracy. The work has been so well known for many years that no specific praise is needed. It is essentially a manual for those beginning work in this field. The author has kept this purpose in view, and hence has wisely refrained from increasing materially the size of the book by incorporating any considerable part of the great amount of new matter that has of late been added in the field of oils, vegetable, animal and mineral. The changes in the present edition are the addition of a section on examination of motor gasoline and a description of the MacMichael Absolute Viscometer. The author thinks that modifications will be later needed in both these descriptions and they are placed provisionally in an appendix. Printed in compact form and descriptions condensed, but still quite clear, the book contains a large amount of matter on a subject of great importance to all concerned in chemical or mechanical industries.

HENRY LEFFMANN.

VAN NOSTRAND'S CHEMICAL ANNUAL. A Handbook of Useful Data for Analytical Manufacturing and Investigating Chemists, Chemical Engineers and Students. Edited by John C. Olsen, A.M., Ph.D., assisted by T. R. LeCompte, B.A., M.S. Fifth issue, 1922. 886 pages and index, small 8vo. New York, D. Van Nostrand Company, 1922. Price $4.00 net.

This work has been known and used by chemists and correlated workers for eighteen years, and requires no encomiums from the reviewer. Such compilations are of great value to all engaged in laboratory or manufacturing operations. The data that have been accumulated concerning the properties of substances are scattered through thousands of publications many of which are inaccessible to the mass of chemists, and the bringing of these together in a convenient form is a most useful service. Of course, the value of such a work will depend largely on the thoroughness with which the literature is searched and the care taken in the selection of material. These requirements have been fully met in the book in hand. Many tables are given and also much descriptive matter. The list of new books covers over eighty pages, including some recent publications in France and Germany. The sizes and prices of those printed in English are given which is an accommodation. In some cases, however, it seems that books not really "new" are noted. Meldola's "Chemistry of Photography," dated 1889, is listed. This can hardly be called a "new book," and while it was a valuable and useful work in its day, it is essentially out of date, in view of the progress that has been in photographic procedure. It is true that some of the fundamental problems of photography, such as that of the latent image, are still obscure, but many new methods have come into use since 1889, and a work on the chemistry of photography should cover these.

The Annual is excellently printed with good type and paper and bound so that it lies open at almost any page.

HENRY LEFFMANN.

CHEMICAL ENGINEERING CATALOG 1922. Seventh annual edition, 1183 pages, 4to, flexible cover. New York, The Chemical Catalog Company, Inc., 1922. Price $10.00 net.

This comprehensive volume is the official standard work of reference for all those concerned in the establishment and operation of the chemical industries, and industries in which chemical processes are incidentally a feature. The growth of industries involving the application of chemical or physico-chemical methods has been enormous in the last quarter of a century and the indications are that it will continue at an increasing ratio. The volume is issued annually under the supervision of a committee composed of members of the American Institute of Chemical Engineers, the American Chemical Society and the Society of Chemical Industry, but these committeemen have no financial interest in the work, merely giving time and attention to it in the interest of the purposes for which it is printed.

A work of this character is always useful, in fact, indispensable to the satisfactory development of a nation's industries, but it is especially useful at the present time when the needs of developing American chemical industries are so urgent. A somewhat unusual plan has been adopted of providing for the leasing of the book instead of selling it, the fee for such lease being very trifling. The privilege is, however, limited to certain classes; to those not in such groups, the work is sold outright.

The preface contains a great deal of information concerning the distribution of the work and among other matters it is stated that 11,000 copies of the present edition have been distributed. By furnishing to all firms that carry space a printed list giving the names and addresses of those to whom the book is distributed the value of the compilation is greatly increased. The book is really a wonderful compilation. It is, of course, abundantly illustrated, and being printed on fine paper with clear type and with excellent taste in the display portions, it constitutes a most interesting demonstration of the high degree of efficiency and extensive specialization that the mechanical and chemical interests have undergone. The binding is flexible and permits the book to lie open flat at any page.

HENRY LEFFMANN.

PUBLICATIONS RECEIVED.

The Origin of Spectra, by Paul D. Foote, Physicist, U. S. Bureau of Standards, and F. L. Mohler. American Chemical Society Monograph Series. 250 pages, illustrations, plates, 8vo. New York, The Chemical Catalog Company, 1922. Price $4.50.

The Mechanism of Lubrication. A popular explanation of the principles of lubrication as developed mathematically by Reynolds and Michell, and employed by the latter in the design of the well-known Michell Thrust and Journal Bearings, by William Stone, late Chief Electrical Engineer, Victorian Government Railways. Melbourne, "Industrial Australian and Mining Standard," 1922. Price 2 shillings, 9 pence.

U. S. Bureau of Mines: Bulletin No. 199, Experimental Production of Alloy Steels, by H. W. Gillett and E. L. Mack. 81 pages, plates, 8vo. Technical Paper 290, Inclusions in Aluminum-Alloy Sand Castings, by R. J. Anderson. 25 pages, plates, 8vo. Washington, Government Printing Office, 1922.

Outlines of Theoretical Chemistry, by Frederick H. Getman, Ph.D. Third edition, thoroughly revised and enlarged. 625 pages, illustrations, 8vo. New York, John Wiley and Sons, Inc., 1922.

Van Nostrand's Chemical Annual. A hand-book of useful data for analytical, manufacturing and investigating chemists, chemical engineers and students. Edited by John C. Olsen, A.M., Ph.D. Fifth issue, 1922. 900 pages, plates, portrait, 12mo. New York, D. Van Nostrand Company, 1922. Price $4.00 net.

A Short Handbook of Oil Analysis, by Augustus H. Gill, S.B., Ph.D. Revised tenth edition. 223 pages, illustrations, 12mo. Philadelphia, J. B. Lippincott Company, 1922.

Mechanical Laboratory Methods. The testing of instruments and machines in the mechanical engineering laboratory and in practice by Julian C. Small-wood. Third edition, revised and enlarged. 423 pages, illustrations, 12mo. New York, D. Van Nostrand Company, 1922. Price $3.50 net.

National Advisory Committee for Aeronautics: Technical Notes, No. 110, The Effect on Rudder Control of Slip Stream Body, and Ground Interference by H. I. Hoot and D. L. Bacon. 7 pages, illustrations, photograph, quarto. No. 112, The N.A.C.A. Three-component Accelerometer by H. J. E. Reid. 6 pages, illustrations, photograph, quarto. No. 113, Report on the General Design of Commercial Aircraft by Edward P. Warner. 19 pages, illustrations, quarto. No. 114, Supplementary Report of Oil Scraper Piston Rings by H. S. McDewell. 8 pages, quarto. Washington, Committee, 1922.

U. S. Department of Agriculture: Department Circular 226, White-pine Blister Rust in the Western United States. Contribution from the Bureau of Plant Industry. 7 pages, illustrations, colored plates, 8vo. Washington, Government Printing Office, 1922.

Sound Absorption Measurements. PAUL E. SABINE. (*Phys. Rev.*, April, 1922).—It will be recalled that Professor Sabine of Harvard measured the absorbing power of sound waves of unit areas of various substances. Beneath his calculations lay the assumption that the total absorbing power of a number of articles, such as an assemblage of cushions, was in proportion to their total area. This now seems to lack justification at least in the case of highly absorbent materials. For these the apparent absorbing power per unit area appears to depend on the area and shape of the sample tested as well as upon its position in relation to other absorbing surfaces, provided the dimensions of the sample are not large with respect to the wave-length of the sound employed. With felt the absorbing power of each square metre grew less as the total area of the material exposed in the Sound Chamber of the W. C. Sabine Laboratory was made greater. Long narrow pieces manifested a larger absorbing power per unit area than equal areas in the form of a square, the ratio in the most striking case being about 3 : 1. It may be that diffraction has no inconsiderable part in such effects.

G. F. S.

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HIGH-SPEED PHOTOGRAPHY OF VIBRATIONS (SOUND, MECHANICAL, ELECTRICAL, ETC.).*

BY

AUGUSTUS TROWBRIDGE, Ph.D., D.S.M., D.S.O., Chev.L.H.

Professor of Physics, Princeton University, Princeton, New Jersey.
Member of the Institute.

Up to within a few years ago I shared what I believe to be the general feeling among technical scientific men that photographic methods of recording experimental data such as pressure-volume changes in engine cylinders, motion or timing of valves, vibrations of sonorous bodies, motions of optical images or the interference fringes obtained with visible or ultra-violet light, etc., etc., could not be rendered sufficiently simple to be reliable in the hands of the ordinary intelligent mechanic. Nearly two years' experience in France during the war convinced me that photographic recording is the quickest, cheapest, most simple and cleanest method there is. In the American Army I was in charge of the sound-ranging service, the object of which was to locate the positions of the enemy large calibre guns by recording the time of arrival of their sound at known positions near our own trenches. An accuracy of about fifty feet in five miles was required and a delay of more than four or five minutes in recording, calculating and reporting to our own artillery headquarters was considered excessive. The work was carried on by the ordinary enlisted man who had been given but a few weeks' special

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training; and it was always conducted under rather unfavorable conditions in cellars of ruined houses or in crowded dugouts. I believe that photographic methods which stood this test continually for months without a breakdown are suitable for use under almost any conditions.

Success was chiefly due to the fact that all operations were made strictly automatic. The camera was designed to use a cheap sensitized paper which was fed from a 200-foot roll past a stationary lens through which the exposure was made. The paper was automatically developed and fixed before it left the camera, so that there was no chance whatever of confusion of records when a great many were being taken in rapid succession, since the operator could inspect and mark with a pencil each record as it issued from the camera. In the case of the camera originally designed for field use, the speed of taking the photograph was slow, so that the paper could be run through the developer and fixer at the same speed at which exposure was made, without danger that the development might not be long enough for the most satisfactory contrast between light and shadow. For laboratory purposes, however, it is desirable that very rapid exposures may be taken in some instances and therefore the camera was re-designed by Mr. William Duryea, head mechanician of the Physical Laboratory of Princeton University, whose great experience in the design and construction of the field instrument enabled him to retain the excellent simple automatic features which had been thoroughly tested, and, at the same time, introduce modifications which permit much greater flexibility in use. One of these is a simple mechanism which allows the record to be taken at one speed and developed at a slower speed so as to give sharp contrast. Exposure speeds up to about four feet per second, using an ordinary automobile electric-light bulb as a source of light, can be used and the automatically developed records show entirely satisfactory contrast.

A series of fine lines reaching clear across the paper is photographed at the same time as the record. These lines are spaced 0.01 second apart, even if the speed of the paper should vary slightly, and serve as time-lines to time accurately an event shown on the record; for example, the opening and closing of an exhaust-valve of a running automobile engine.

An automatic recording camera can be used to trace the motion of any moving part of a mechanism and, owing to the high speed at which a record can be taken, it is possible to study variations which occur in time-intervals as short as 0.001 second. It is more convenient to transmit electrically to the camera the motion that actually takes place in the mechanism than to attempt to set up the camera itself close to the mechanism. A special form of simple string galvanometer is very convenient and meets satisfactorily the necessary condition that its moving part shall move synchronously with the motion of the mechanism. The moving part of the galvanometer is practically weightless, as it is a short piece of wire 0.0004 inch in diameter, and its motion is strongly damped by the magnetic field in which it is placed. When a current is sent through this wire it moves in the magnetic field and a shadow of this motion is photographed by the automatic camera.

In practice, almost any slight motion can be converted into a flow of electricity, so that the applications of photographic recording to the study of vibrations in running machinery are very numerous.

CAMERA.

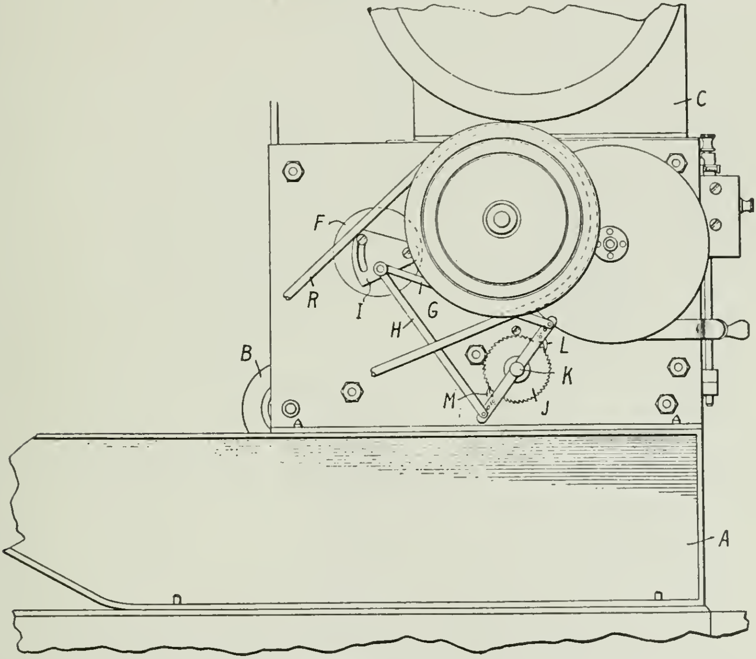
The essential features in the design of a suitable photographic recorder for the experimental purposes of a laboratory are somewhat similar to those embodied in the moving picture machine, in that a sensitized tape must be moved rapidly behind a suitable lens which brings an image of the moving object on the sensitized tape. In the moving picture camera an extended image of a variety of objects must be formed and a series of such extended images is obtained by the use of a shutter which revolves at suitable speed. The problem is somewhat simpler in the design of photographic recorder since the moving object which is to be photographed is, in general, very small compared to the moving objects photographed by the moving picture camera. It is, in fact, generally possible to arrange that the moving object shall be a point of light, or, at least, a fine line of light, whose long dimensions may be brought parallel to the direction of motion of the sensitized tape in the camera. Instead of a line or point of light, a sharply defined moving shadow caused by the motion of a very fine wire may be the object to be photographed. Under these conditions there is not the possibility of overlapping of portions of the images on the sensitized tape that there would be in the moving picture camera and hence the usual shutter of such cameras may be dispensed with and an actual continuous record of the motion of the small body may be made instead of a series of instantaneous photographs of its position as would be the case were a shutter used. The possibility of doing away with the shutter greatly simplifies the design and permits the attainment of very rapid exposure without any serious mechanical difficulty.

If it is desired to record the motion of a spot of light which moves, say, in a horizontal plane, an ordinary lens may be used to bring an image of the spot on the moving sensitized tape and the tape is run rapidly behind the lens in a vertical plane. This gives a photographic trace of the position of the spot in the form of a line. If a bright flash or a dense shadow is thrown across the tape every hundredth of a second, for example, it will be possible to tell from the developed record just what the position of the spot of light was at any given instant of time. If, instead of a spot of light, the moving object is a fine line of light or a sharply defined shadow in a vertical plane, it is necessary to substitute for the ordinary lens, to bring the image on the tape, a cylindrical lens whose axis (the axis of the cylinder from which the lens is cut) lies in a horizontal plane. The action of such a lens is to gather all of the light from a vertical line and focus it into a very bright and tiny spot and the lens has no condensing action in the direction of its own axis; therefore, the line of light is imaged as a spot of light whose diameter is the correct image of the diameter of the line of light. If there is no motion of the line the photographic record is a straight line which is the correct image of the stationary line. If the line moves rapidly the record shows a curve any point on which is the image of the position of the moving line at the corresponding time. If a sharp shadow is cast by an opaque narrow wire which moves, the motion of that shadow gives a curve on the record which is a faithful representation of the motion of the wire which casts the shadow.

Figs. 1, 2, and 3 show some of the especial features of a recording camera.

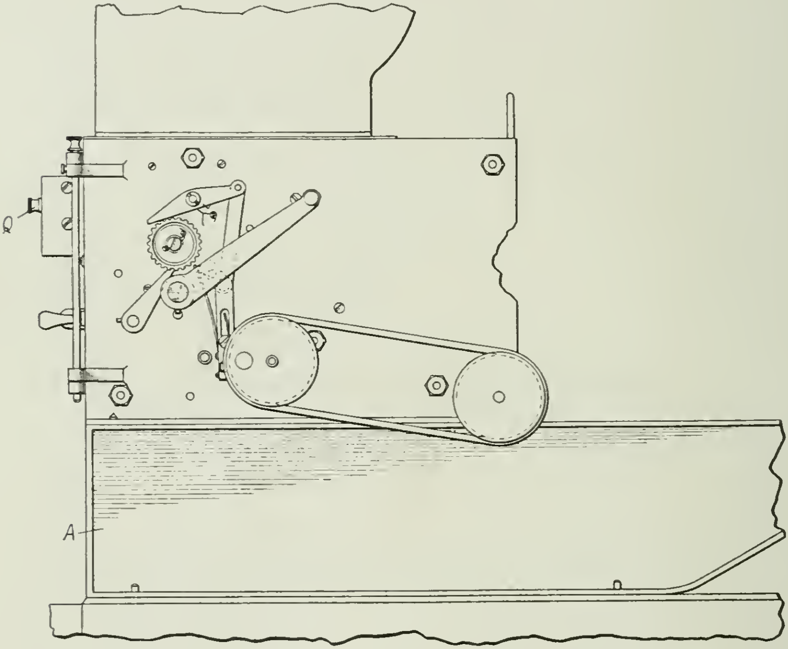
In Fig. 1, A is a trough with two compartments which serves as a base to the camera. In the compartment which extends from the extreme right of the figure to a point below B the developer is placed. B is a roller which transfers the developed film into the second portion of the tank to the left of the figure in which the fixing bath is. The developed side of the film is the under side as it comes through the baths, and, for this reason, is sufficiently protected from daylight so that the fixing may be done outside the camera proper. The unexposed film is stored in the upper cylindrical portion of the camera (shown in part near C) and is fed down in a vertical plane at the right of Fig. 1, being caught by the rollers D shown in Fig. 4 (in plan). If the speed of exposure is rapid, the rollers D are driven more rapidly than the rollers E by the mechanism shown at F to M inclusive in Fig. 1, which allows of any practical ratio of speeds. When the sensitized tape is started it immediately commences to be fed into the developer at the slower speed and the excess of tape is stored up in a storage space near the top of the camera. The tape passes between the blades of a knife operated by the lever N of Fig. 3, which cuts off the tape when the operator

FIG. 1.



has finished an exposure. When this happens the rollers D, Fig. 4, cease to feed the unexposed tape, but the rollers E and O continue to feed the exposed tape through the solutions until all has passed through. The mechanism, shown enlarged in Fig. 3, serves to guide the tape into the storage space and prevent its entanglement with a new length of tape in case it is desired to expose a second tape before the first one has passed through the camera. The face of the camera is closed by a hinged door—P, Fig. 4—which carries the cylindrical lens with its axis in a horizontal plane. The amount of light admitted to the lens is regulated by a horizontal aperture of variable width which can be opened or closed by a knurled screw Q, Figs. 2 and 4. The power necessary to drive the mechanism is supplied by a motor (not shown) which may be started or stopped by a foot switch controlled by the operator. This motor drives the mechanism by means of a belt R. Suitable gears, shown in Fig. 4, are used to drive the roller D at any desired speed.

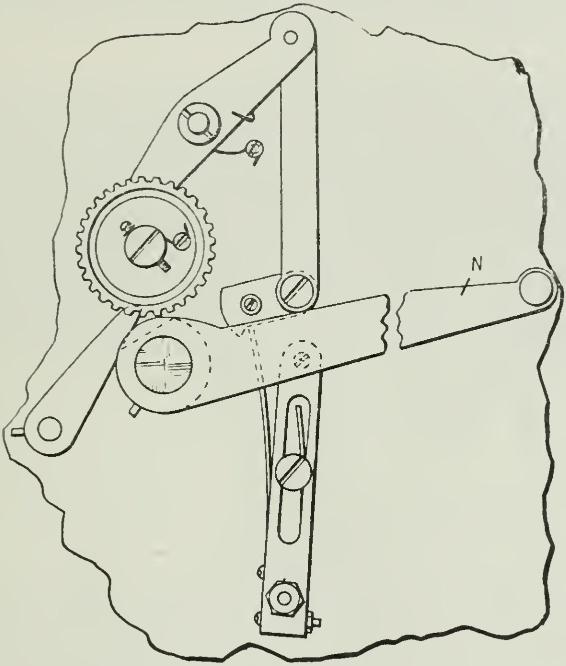
FIG. 2.



TIME SCALE.

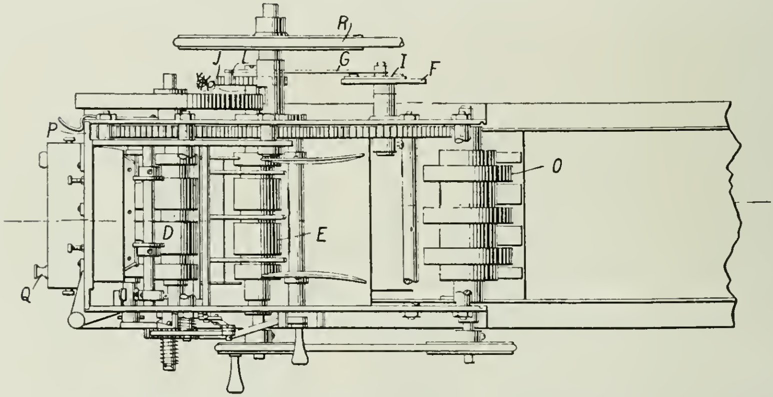
It is perfectly possible to feed the sensitized tape through the camera at practically constant speed, so that linear distances along the tape are approximately proportional to the time. However, it is easily possible to photograph on the tape itself an exceedingly accurate time scale in the form of lines across the record at right angles to the direction of motion of the tape. This may be done by causing a spoked wheel to revolve rapidly in the path of the light with which the record is photographed. The rotation of this wheel may be governed by the motion of the prongs of an electrically driven tuning fork in such a way that a spoke of the wheel is brought parallel to the axis of the cylindrical lens at intervals of exactly one one-hundredth of a second. The shadow thrown by a spoke may be made to completely block off all light as the spoke comes into parallelism with the axis of the cylindrical lens and a sharp image of this shadow may be formed on the sensitized tape by means of an ordinary lens placed between the spoke and the cylindrical lens. By this means an

FIG. 3.



accurate time scale may be photographed on the tape at the same time as the record of the motion which is being photographed by the cylindrical lens is being made. In this way the accuracy of the time scale is in no way affected by unsteadiness of motion of the tape, since, were the motion to slow down due to friction, the spacing of the time lines would be less in distance but still the same in time interval. This devise is an old one known as the phonic wheel and has been used extensively in physiological and psychological apparatus though it has seemed to have found little use in physical apparatus. It leaves very little to be desired on the score of accuracy and, on the score of simplicity and dependability, nothing could be better.

FIG. 4.

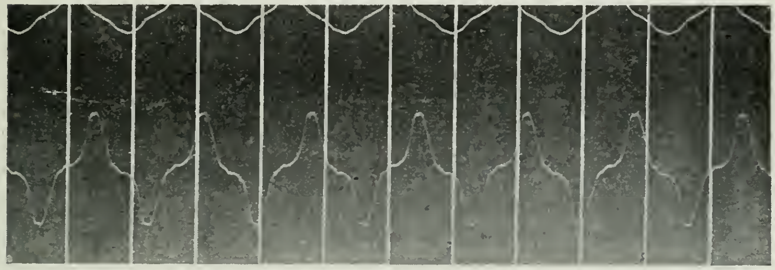


GALVANOMETER.

With the recording camera just described a great variety of motions may be photographed directly. A fine wire may be attached to the moving part and suitable illumination provided and a motion of the shadow of the wire photographed. Often it is more convenient to convert the motion which it is desired to record into a flow of electric current, to pass this current to a suitable galvanometer and to record the motion of the moving member of this galvanometer. If this is done, great care must be taken that the galvanometer used must not introduce motions characteristic of itself. The moving part of a suitable galvanometer must execute motions which are determined practically only by the current flowing and not at all by the inertion or elastic properties of the moving part of the galvanometer. That is, the moving part must be practically without weight, it must have a restoring force acting on it which will make it return quickly to its position of rest, and its motion must be sufficiently damped so that it will not tend to overshoot its position of deflection as it takes up this position. In addition, it must be moderately sensitive so that small currents may produce appreciable motions.

It is impossible to fulfill all of these conditions absolutely, but they have been practically met in the design of the string galvanometer by the Dutch physiologist, Einthofen, and described by him in *Pflüger's Arch. f. d. Gesamte. Physiol.* (**99**, p. 472, 1903).

FIG. 5.

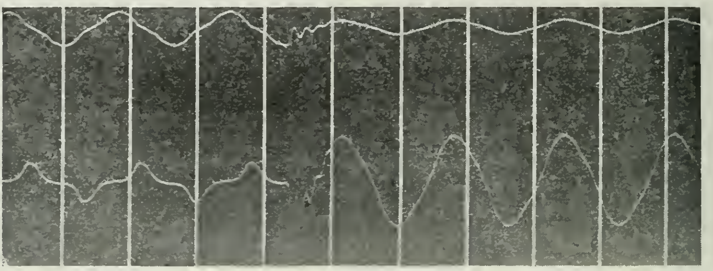


The full theory of the design and performance of the string galvanometer is also given in *Ann. der Phys.* (**21**, 1906, p. 483).

The instrument which I have used in connection with the recording camera is a simple modification of the Einthofen instrument. One or more very fine wires are mounted vertically between the poles of an electromagnet whose magnetic field is horizontal. The pole pieces of the magnet are bored out and each is fitted to carry a small microscope objective lens of about ½-inch focus, each lens being about ½ inch from the plane of the fine vertical wires. Light passing through the lenses travels at right angles to the plane of the vertical wires and along the lines of force of the magnetic field.

As a source of light a small nitrogen filled tungsten filament automobile head-light bulb is used. A small lens forms a real image of the filament at ½ inch from the first microscope objective mentioned above. Between the bulb and the small lens a spoked wheel is mounted so that the spokes, as they revolve, cut off the light. The spoked wheel is rotated at constant speed, so that a spoke comes into a horizontal position every hundredth of a second. The constancy of rotation of the wheel is secured by governing its motion by current impulses from an accurate tuning fork, itself electrically driven. The light from the real image of the tungsten filament is rendered parallel by the first microscope objective and this narrow parallel beam of light illuminates uniformly the vertical fine wires of the galvanometer. These wires cast shadows which may be focussed by the second microscope objective so as to be sharp black lines in the plane of the photographic tape of the camera. A cylindrical lens is mounted in the converging beam of light so as to render the sharp shadow lines sharp shadow points as mentioned above.

FIG. 6.

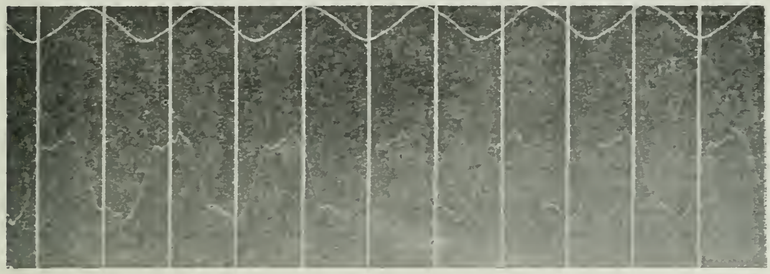


When a current flows in one of the galvanometer wires, the wire moves at right angles both to its own length and to the direction of the magnetic field in which it stands, and since the beam of light is in the direction of the magnetic field, the motion of the wire is in a vertical plane and across the beam of light. The shadow of the wire will thus move across the axis of the beam of light or will move in the plane of the sensitized tape of the camera. For small currents the amount of motion of the point image of the shadow on the tape will be proportional to the current and a reversal of the direction of flow of current in the wire will produce a reversal of the motion of the shadow. It is possible to adjust the position of the wire in the magnetic field of the galvanometer so that the deflection of the shadow to the right and left of the zero position is accurately the same when a given current is sent, first in one direction and then in the other, through the galvanometer wire.

DAMPING.

If a small current be sent through the wire and a permanent deflection of the shadow image obtained, and then the circuit be suddenly broken, the record of the motion of the wire as it returns to its zero position is a wave motion whose period is determined by the tension to which the wire is subjected and by the mass of the moving wire. The successive excursions of the wire about its zero position grow gradually less because of air friction, stiffness of the wire, etc. The motion of the wire on open circuit is only very slightly damped and the instrument would be wholly unreliable if used under these conditions, for the motions of the wire would be more characteristic of the tension and mass of the wire itself than they would be of the current flowing in the wire. The behavior of the wire will be quite different, however, if it is always shunted with a resistance comparable to its own resistance, for then, as the wire moves in the magnetic field it acts as a tiny dynamo and sends current through the shunting resistance, and the energy of this induced current must come from the motion of the wire. To the small air friction damping which exists when the wire is on open circuit, is added a large electromagnetic damping when the wire is shunted with a resistance comparable to its own resistance and the amount of this electromagnetic damping may be increased by reducing the resistance of the shunt. In practice it is possible to render the motion of the galvanometer wire practically aperiodic by the use of a shunt whose resistance is about one-third of that of the wire itself. This has the disadvantage of reducing the sensitivity of the galvanometer to about one-third of what it would be were no shunt used, but the gain in having a practically dead-beat instrument whose motion depends solely on the instantaneous value of the current flowing in it, more than offsets this sacrifice in sensitivity.

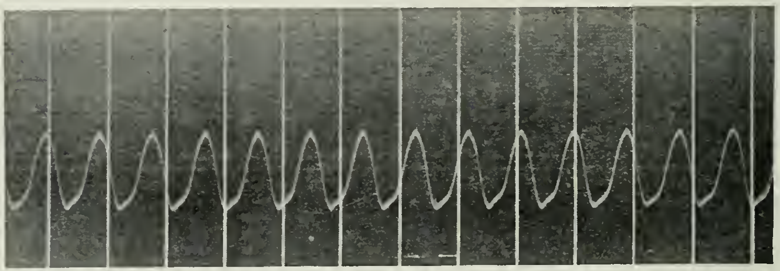
FIG. 7.



If one wishes to record very rapid variations in current, one must put the wire under rather strong tension so that its free period (undamped) shall be less than the period of the current variations one wishes to record; at the same time one must shunt the wire with small resistance in order that the motion of the wire may be sufficiently damped so as to be practically aperiodic. Under these conditions the sensitivity of the instrument (deflection for a given current in the wire) will be relatively small, both because of the large tension and because of the low shunt.

If one has to record slow variations in current, one may relax the tension and secure adequate damping by the use of a higher resistance shunt and the sensitivity under these conditions may be relatively very large.

FIG. 8.



It follows from these considerations that the electromagnet of the galvanometer should be designed to give as strong (and uniform) magnetic field as possible in the region where the wire (or wires) stands since both the sensitivity and the damping increase with increasing field strength. In the instrument constructed in this laboratory, great care has been given to this element in design and the results are very satisfactory since it is possible to obtain a sensitivity of about one one-hundred thousandth of an ampere per millimetre deflection of the shadow of the wire and still preserve sufficient quickness of response and damping to faithfully record small current variations as rapid as a few hundred per second.

So great a sensitivity as this is not needed for most laboratory purposes. When it is not needed a faithful record of current variations taking place in less than a thousandth of a second may be easily secured by increasing the tension and damping of the wire.

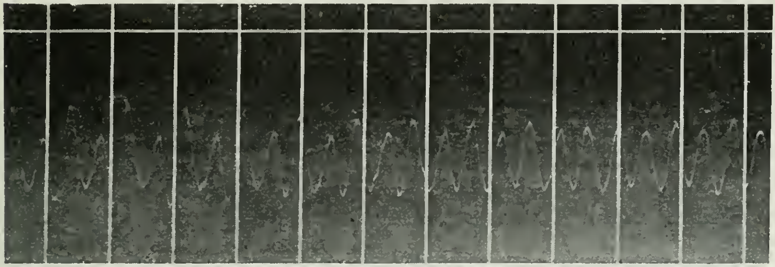
Examples of Use of Recorder.—

(*a*) As an oscillograph for current and voltage measurement with alternating currents.

If two wires are used, one may serve to record variations in electromotive force and the other to record current variations.

Fig. 5 shows a record of the voltage over the primary of small, cheap transformers with an iron core, and the current in the primary when the secondary is on open circuit. (In the following figures the voltage record is at the top and the current record near the middle of the tape and the beginning of the record is at the left-hand edge, so that each line on the time scale as one counts towards the right, is one one-hundredth of a second later than the line to its immediate left.)

FIG. 9.



In this figure it will be noted that the current attains its maximum later than the voltage attains its maximum (*i.e.,* the current lags on the e.m.f. in the inductive circuit) and on measurement it will be seen that the lag is very nearly one-quarter of a period. It will be further noted that the current does not follow a simple sine law but shows evidences of hysteresis losses in the iron core of the transformer. Fig. 6 shows the effect of suddenly short-circuiting the secondary of the little transformer by placing a knife blade across its terminals (contact not very abrupt!). The effect is to reduce the impedance of the primary which is shown as an increase in the current and a decrease in the voltage, and to bring the phase of the current into practical agreement with that of the e.m.f. (*i.e.,* to reduce the angle of lag to zero), and also to make the current nearly a sine wave. Fig. 7 is the record of voltage over, and current through, a small telephone condenser of about two microfarads capacity, and the current will be seen to lead on the e.m.f. by about a quarter of a period; also the distorsions of the current wave from the sine form owing to harmonic components for which the reactance of the capacity is less than for the fundamental are easily noticed.

(*b*) Records of Musical Notes.

In Figs. 8, 9 and 10 are shown records of the flow of current in an ordinary telephone microphone when an open organ pipe was blown near the microphone. They are thus approximately similar to the wave form of the notes given out by the organ pipe.

Fig. 8 shows the fundamental note of a large pipe giving 113 vibrations per second.

Fig. 9 is another record of the same pipe giving the octave 226 vibrations per second.

FIG. 10.

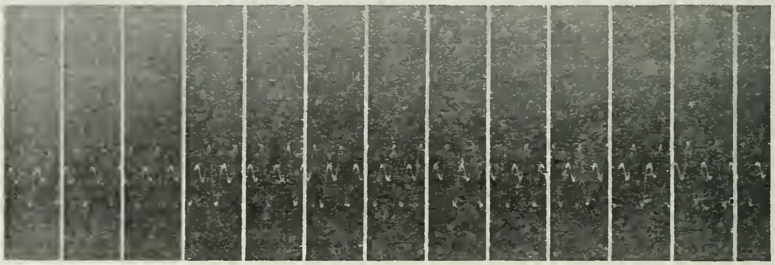


Fig. 10 shows the octave and double octave of the fundamental note of the pipe.

Fig. 11 is a record taken when the pipe was very strongly blown and giving a variety of overtones, the most rapid of which is 904 vibrations per second.

The great regularity with which vibrations repeat themselves is not to be wondered at in the cases shown in records 5, 6 and 7, for the alternating current was furnished by a large engine in a central power station, but the regularity exhibited in records 8, 9 and 10 is rather surprising in view of the fact that the primary curve was a blast of air in an organ pipe. Not only the frequency remained constant, but also the quality of the note remained the same in succeeding vibrations.

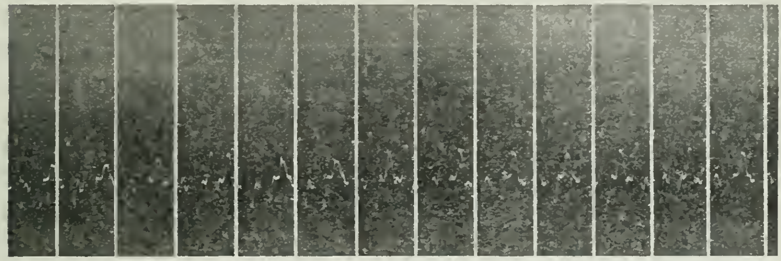
(*c*) Records of pressure and volume changes in cylinder of high-speed internal combustion engines.

The recorder has been used with considerable success in the study of the causes of the " fuel knock " in automobile engines.

To discuss details would lead beyond the scope of this paper, but one or two points about the design and construction of suitable indicators for measuring rapid changes in pressure will not be out of place.

What has been said above about the necessity of securing aperiodicity in the wire of the galvanometer described in this paper holds with equal force in the case of the design of a suitable indicator to record rapid fluxations of pressure: The indicator must indicate the pressure to which its moving part is subjected, and it must not have any mechanical peculiarities of its own which might be mistaken for true pressure variations. In other words, it must be sufficiently damped so that its motions are aperiodic, and it must be stiff so as to have a quick period of return to its position of rest. One way in which these properties may be obtained is to have a small capsule fitted so as to screw into a pet cock opening of a cylinder and to close the other end of the capsule with a stiff disk of steel. A second capsule above the steel disk may be designed so as to insure that the disk as it moves shall move a quantity of air or other fluid through narrow passages in order to provide some damping action to the motion of the disk. The entire double capsule is water-jacketed so as to prevent heating due to the hot gases on the side of the disk next to the engine cylinder. The disk may be shaped so that its bending (if small) is proportional to the pressure exerted by the hot gases in the cylinders.

FIG. 11.



Indicators built on this principle have been in use for some time. Most of these have measured the bending of the disk either by the use of a train of delicate levers or by a combination of levers to move a mirror from which a beam of light is reflected to a photographic plate. These methods are not free from theoretical and practical difficulties since it is difficult to insure that the levers themselves do not introduce lost motion and so produce vibrations in the record which are not due to pressure changes in the cylinder, and moreover, any recording mechanical indicator attached directly to a running engine shares the not inconsiderable vibration of the engine itself and, unless it is very massive and rigid, is likely to give a record on which the mechanical vibrations are impressed on the pressure changes it is designed to record. Massive construction of the recording indicator is an undesirable feature for the reason that quick changes from one cylinder to another of a running engine are rendered difficult.

It seemed to me, therefore, desirable to retain the disk form of indicator and eliminate the objectionable lever feature and, naturally, I thought of converting the motion of the moving disk into the flow of electric current and recording this current flow with the recording galvanometer described above. This would allow the indicator proper to be small and easily screwed into a pet cock opening and it would allow the recording part of the apparatus to be set up at a distance from the noisy running engine. To secure this, all that was necessary was to fasten a very small coil of fine wire to the disk and into the coil to place one pole of an electromagnet, the other pole of which was a ring which surrounded the outer circumference of the coil of fine wire. In this way, when the disk moved, it moved all the turns of the fine wire coil across a radial field of magnetic force and an electromotive force was generated proportional to the velocity with which the disk moved. If the coil of fine wire was connected so as to send current through the wire of the galvanometer, this current, and hence the motion of the galvanometer wire, was proportional to the *velocity* of motion of the indicator disk, but the *velocity* of this disk is proportional to the *rate of change of pressure* occurring in the cylinder, so the final result was that the photographic record obtained gave the time rate of change of the pressure in a cylinder at every instant of time. A conveniently placed make-and-break key, placed on the crank shaft of the engine, could be used to send a small current to a second wire in the galvanometer and thus the times at which the cylinder was at any part of its stroke (say in-centre) could be recorded at the same time that the pressure variations were recorded. From these data the pressure corresponding to any given volume of gas in the cylinder can be calculated. However, in a study of changes brought about by changed mixture-strength, changed engine speed, changed temperature or the like, it is not necessary to convert the observed data into the well-known pressure-volume diagram, for one soon becomes expert in interpreting the observed diagram which gives time rate of variation of pressure as a function of time. In fact, such an indicator diagram shows far more of what is going on in an engine cylinder than the corresponding pressure-volume diagram with which engineers are more familiar. One reason for this is that the most interesting part of the cycle of an internal combustion engine is near the in-centre and out-centre positions, for near the former the ignition takes place and near the latter the exhaust valve opens. The standard pressure-volume diagram is most crowded together at these very points, whereas a pressure-change-time diagram is perfectly uniformly spaced. The pressure-volume diagram is widely spaced in the very region where one could stand crowding without sacrificing accuracy and is so crowded together as to be inaccurate at the very places where the most important changes are going on in the cylinder. The pressure-volume diagram was designed for use with slow-speed steam engines and has certain obvious advantages, but it should be discarded when one wishes to represent what goes on in a high-speed internal combustion engine.

In the interests of fuel economy, it is very desirable that far-reaching studies be made looking towards increasing the efficiency of the automobile engine. Automobile engineers should not overlook the fact that the design of efficient steam engines was greatly aided by the perfection of a suitable indicator and that, while the problem of design of an indicator suitable for the high speeds of the internal combustion engine is difficult, it is by no means impossible.

Short Electric Waves. E. F. NICHOLS and J. D. TEAR. (*Phys. Rev.*, July, 1922).—By using the famous Hertzian oscillator with the addition of certain new features it has become possible to produce at will waves of length 1.8 mm. The shortest obtained was .8 mm. in length, but this was not reproducible. It is interesting to note that in two cases Nichols, in collaboration with another physicist, has expanded and perfected the work of Peter Lebedew, *viz.*, in the measurement of the pressure of light and now in the production of short electric waves. G. F. S.

Breath Figures. T. J. BAKER. (*Phil. Mag.*, October, 1922).—"If one breathes upon a sheet of glass which has been cleaned with soap and water and polished with clean linen, water-vapour condenses uniformly on the glass in such manner that the surface as seen by reflected light appears dull and rather white. If the tip of a small blowpipe-flame is made to traverse the surface of such a plate and the plate is then breathed upon as soon as it is cold, a whitish deposit appears on those parts which the flame has not touched, whilst the track of the flame is marked by a form of condensation which, owing to its transparency, appears black by contrast with the neighboring parts." A generation ago this phenomenon was discovered but its cause is not yet known. The extent of our knowledge of this subject is greatly increased by the studies made public in this paper. It is found that not glass alone but also porcelain, rock-crystal, mica, Iceland spar, platinum, nickel, silver, brass and mercury can be used. Aitken suggested that a change in the character of the surface is responsible, but this cannot be true since platinum and rock-crystal act as glass does. Again, a blowpipe-flame might well leave a slight solid deposit on its path over the glass, but this deposit is not necessary for the formation of breath figures since a hydrogen flame is just as effective. On the other hand, the figures are not obtained at all, or at most, to an imperfect extent, when chemically cleaned glass is used. The treatment with soap and water and linen leaves something on the surface that is needed for the production of the effect, and the flame removes some or all of this.

The most striking discovery of the author is that the condition that makes one glass plate capable of showing breath figures can be transferred to another. A plate that had been traversed by a flame was put in contact with another that had not been so treated. "Next day the plates were separated, and it was observed that both plates gave breath figures, one being an exact copy of the other. Moreover, the original showed no diminution of intensity." Later it was found that only a few minutes were needed for the perfect transfer when the plates in contact were under low atmospheric pressure. Even with an interval of 2 mm. between the plates a transfer was obtained. In one case a plate produced a transfer eighteen days after it had been treated with a flame. "Since the process is hastened by reduction of pressure and by rise of temperature, and occurs even when the plates are not in contact, it is clear that some gaseous material passes from one to the other." In spite of his long familiarity with the effect and of his intimate acquaintance with all that is known concerning it, he is unable to present a theory of the phenomenon that is satisfactory to himself. He has varied the surface on which the figures form and the nature of the flame. Why not employ for the third stage of the process something not so complicated in its origin as the human breath? G. F. S.

A STUDY OF NITROCELLULOSE.*

BY

EUGENE C. BINGHAM, Ph.D., and WILLIAM L. HYDEN, M.S.
Lafayette College, Easton, Penna.

INTRODUCTION.

THE experiments of Bingham and Durham[1] with suspensions of infusorial earth, clay, and graphite in water and in ethyl alcohol seemed to prove that the fluidity is a linear function of the concentration; and that independent of the temperature, there is a certain concentration at which the material exhibits zero fluidity. This concentration seemed sharply to demarcate viscous from plastic flow. This conclusion seemed to be confirmed on analysis of the data on asphalt in benzene by Richardson,[2] sulfur in water by Oden,[3] malt flour in water by Lüers and Schneider,[4] sodium palmitate in water by Farrow,[5] glycogen in water by Bottazzi and d'Errico.[6]

At one time there seemed to be no escape from this reasoning, but recent knowledge of plastic flow necessitates our viewing with suspicion all viscosities of colloidal solutions where the flow was measured at a single shearing stress; for it has been shown[7] that in many instances a change in the shearing stress will entirely change the magnitude of the apparent fluidity. In order to measure the fluidity of a liquid, it is therefore necessary to use two or more shearing stresses, provided that there is any question as to whether the liquid is a colloidal solution or not.

It has been abundantly proved by many experimenters that, in *true solutions,* it is necessary to measure the flow at one shearing stress only in order to obtain the correct fluidity. This fact, however, should not lead us to assume that the same simple relations hold in *colloidal* solutions. For it seems, *a priori,* inevitable that in a given instrument, the material which just seems to exhibit zero fluidity at a given shearing stress will again begin to flow when the shearing force is considerably increased, making possible the calculation of a new and different value for the fluidity. Hence there is reason for believing that fluidities of colloidal solutions as ordinarily measured are really a function of the shearing stress and therefore *apparent fluidities* only. They stand in need of correction in order that they may become truly constants of the material studied. The whole subject is in need of investigation to prove first of all whether the fluidity is a function of the shearing stress, as seems probable.

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* Communicated by Dr. Bingham.

[1] *Am. Chem. J.,* 46, 278 (1911).

[2] "Fluidity and Plasticity," p. 205.

[3] Do., p. 204.

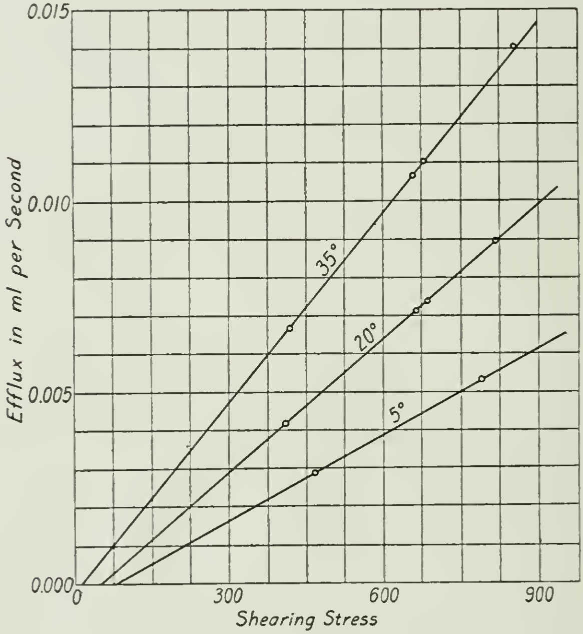
[4] Do., p. 290.

[5] Do., p. 291.

[6] Do., p. 207.

[7] Do., pp. 52, *et seq.,* 240, 279.

FIG. 1.



The efflux-shearing stress curves at 5°, 20°, and 35° for a 7.708 per cent. dispersion of nitrocellulose in acetone.

MATERIALS AND APPARATUS USED.

It seemed best to work with both a suspension—(or non-polar) and an emulsion—(or polar) colloid. As a type of the latter for study in this paper, we have chosen nitrocellulose. It is easily obtainable in a sufficiently pure condition, its so-called "solutions" are quite stable from the physico-chemical point of view, and the results of our investigation promised to have a practical bearing in various industries. The material was pyroxylin, containing 12.11 per cent. nitrogen, kindly supplied us by the E. I. du Pont de Nemours and Company. It was dried for eight hours in an oven at not over 50° C., and thereafter kept in a vacuum desiccator over sulfuric acid.

Acetone was used as the dispersion means, the sample being obtained from bisulfite compound in the Eastman Kodak Research Laboratory and by us merely dried over calcium chloride and distilled. The corrected and reduced boiling point was found to be 57.1° C.

The solutions were made in a 100 ml. flask closed by means of a tight-fitting stopper, and shaken for four hours on a shaking machine. Weighing after the operation was over proved that evaporation had not taken place. The solution was allowed to stand for twelve hours before use, and the clear solution was then carefully pipetted off for use.

THE MEASUREMENTS.

The measurements were made on viscometers Nos. 3, 6 and 7, the use of which has already been sufficiently described.[8] The shearing stress at the wall of the capillary is obtained from the following relation:

$$\pi R^2 P = 2\pi R l F$$

whence

$$F = \frac{R}{2l} P.$$

With a concentration of only 1.39 per cent. by weight of nitrocellulose, the fluidity, at 30° C., was measured in the ordinary manner at three different pressures as measured on the manometer. With a pressure of 403.6 g. per cm.^{2} the fluidity was 52.49, at 214.6 g. per cm.^{2} the fluidity was 51.31, whereas at 62.96 g. per cm.^{2} the fluidity was only 50.76. The difference between the extremes is 1.73, which is 3.3 per cent. of the mean, but the experimental error amounts to only a few tenths of one per cent., so considering the steady increase in the fluidity with the pressure it is made probable that even a very dilute nitrocellulose solution behaves like a plastic material in that the fluidity is a function of the shearing stress.

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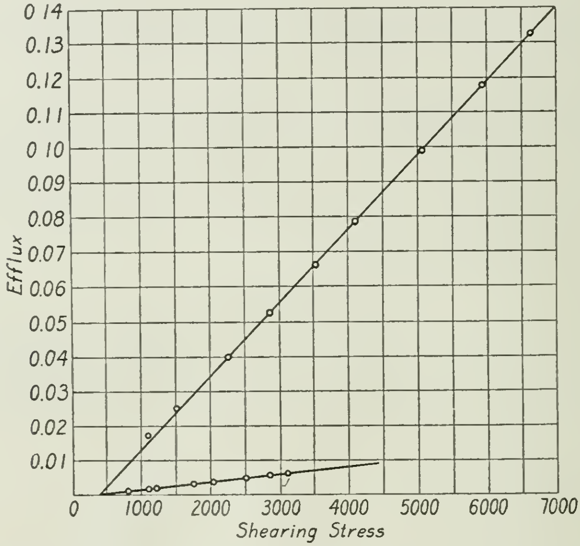
[8] "Fluidity and Plasticity," p. 76.

The efflux expressed in ml. per second is found to be a linear function of the shearing stress (Fig. 1), as has already been found to be the case with many plastic materials. When the shearing stress is extrapolated to its value when the efflux is zero, we obtain the friction or yield value *f*. It may be defined as the shearing stress at the wall of the tube necessary to start the flow, assuming that the curve is linear throughout its entire length.

Fig. 2.



Efflux-shearing stress curves of anti-rust black paint with capillaries of different dimensions. The radius of No. 10 is 0.0147 cm. and that of No. 11, 0.036 cm. The length of No. 10, is 3.05 cm. and that of No. 11 3.04 cm.

The yield value has already been proved to be independent of the length or radius of the capillary through which the flow takes place. Thus Bruce measured the flow of an anti-rust black paint,[9] using capillary No. 10 with a length of 3.051 cm. and a radius of 0.01469 cm. and capillary No. 11 with a length of 3.041 cm. and a radius of 0.03062 cm. By the graphical method the same yield value of 360 dynes per cm.^{2} was found for both, and the mobilities were 0.796 for No. 10 and 0.795 for No. 11 capillary. (Cf. Fig. 2.) The mobility μ is calculated by means of the formula [10]

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[9] *Proc. Am. Soc.,* "Testing Materials," 1922.

[10] "Fluidity and Plasticity," p. 225.

$$\mu = \frac{4V}{\pi R^3 (F-f) t}$$

where V is the volume of efflux in the time t, R is the radius of the capillary and F is the total shearing stress in dynes per cm.^{2}

DATA.

The results obtained are given in the following tables. Three viscometers were used, whose principal dimensions are as follows:

TABLE I.

	Radius of capillary in cm.	Length of capillary in cm.	Volume of efflux in ml.
Viscometer No. 3.........	0.01029	7.5	4.00
Viscometer No. 6.........	0.03202	13.75	4.00
Viscometer No. 7.........	0.03512	13.15	4.00

TABLE II.

The Fluidity of Pure Acetone.

Viscometer No. 3.

Temp. C.	Time seconds.	Press. g. per cm.^{2}	Fluidity.	Spec. Vol.
10°	241.9	103.7	278.8	1.2435
20°	218.7	103.2	309.6	1.2616
30°	199.1	102.6	342.3	1.2804

TABLE III.

Plasticity of 1.073 Per Cent. of Nitrocellulose by Weight in Acetone.

Viscometer No. 3.

Temp. C.	Time seconds.	Shear. Stress Dynes per cm.^{2}	Friction Dynes per cm.^{2}	Mobility.
20°	284.0	256.1	1.5	64.63
20°	271.1	266.0	1.5	65.16
20°	311.1	233.4	1.5	64.75
20°	367.9	198.6	1.5	64.42
20°	454.4	161.8	1.5	64.13
20°	619.0	120.2	1.5	63.43
				64.59 Ave.

TABLE IV.

Plasticity of 1.39 Per Cent. of Nitrocellulose by Weight in Acetone.

Viscometer No. 3.

Temp. C.	Time seconds.	Shear. Stress Dynes per cm.^{2}	Friction Dynes per cm.^{2}	Mobility.
30°	329.9	271.7	1.5	52.40
30°	634.7	144.5	1.5	51.47
30°	2189.2	42.46	1.5	52.04
30°	1003.2	91.23	1.5	50.44
				51.59 Ave.

TABLE V.

Plasticity of 2.743 Per Cent. of Nitrocellulose by Weight in Acetone.
Viscometer No. 7.

Temp. C.	Time seconds.	Shear. Stress Dynes per cm.^{2}	Friction Dynes per cm.^{2}	Mobility.
15°	79.5	147.0	1.5	10.16
15°	185.3	63.99	1.5	10.15
15°	185.3	63.99	1.5	10.15
15°	249.5	47.17	1.5	10.08
				10.14 Ave.

Viscometer No. 6.

Temp. C.	Time seconds.	Shear. Stress Dynes per cm.^{2}	Friction Dynes per cm.^{2}	Mobility.
20°	286.3	48.59	1.0	11.39
20°	155.1	89.21	1.0	11.34
20°	201.0	68.82	1.0	11.41
20°	103.7	131.90	1.0	11.44
				11.39 Ave.

TABLE VI.

Plasticity of 3.98 Per Cent. of Nitrocellulose by Weight in Acetone.
Viscometer No. 6.

Temp. C.	Time seconds.	Shear. Stress Dynes per cm.^{2}	Friction Dynes per cm.^{2}	Mobility.
10°	151.2	316.2	6.0	3.31
10°	260.9	188.4	6	3.33
10°	725.8	69.5	6	3.36
				3.33 Ave.
20°	557.4	69.6	5	4.31
20°	248.7	154.1	5	4.18
20°	154.9	242.9	5	4.21
				4.23 Ave.
30°	120.1	243.3	4	5.39
30°	187.0	158.9	4	5.38
30°	476.0	63.5	4	5.47
				5.41 Ave.
40°	371.3	63.7	3	6.64
40°	371.3	63.7	3	6.62
40°	110.5	208.4	3	6.67
				6.64 Ave.

Table VII.

Plasticity of 4.966 Per Cent. Nitrocellulose by Weight in Acetone.
Viscometer No. 6.

Temp. C.	Time seconds.	Shear. Stress Dynes per cm.^{2}	Friction Dynes per cm.^{2}	Mobility.
20°	314.1	259.8	8	1.96
20°	261.7	309.0	8	1.97
20°	510.0	162.9	8	1.93
20°	1342.6	63.1	8	2.09
				1.99 Ave.
35°	579.0	97.6	4	2.85
35°	319.1	174.6	4	2.86
35°	181.7	299.6	4	2.89
				2.87 Ave.

Table VIII.

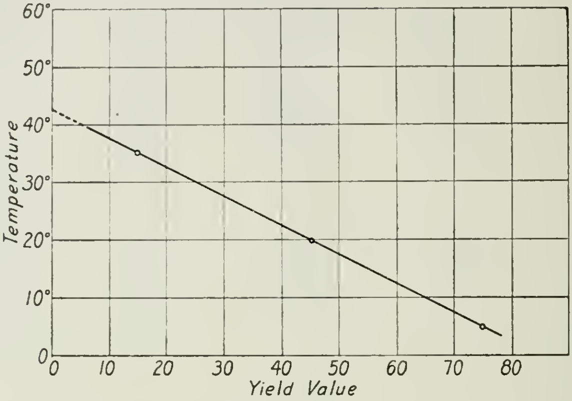
Plasticity of 7.708 Per Cent. of Nitrocellulose by Weight in Acetone.
Viscometer No. 6.

Temp. C.	Time seconds.	Shear. Stress Dynes per cm.^{2}	Friction Dynes per cm.^{2}	Mobility.
5°	1373.0	464.6	75	0.290
5°	744.6	797.3	75	0.288
				0.289 Ave.
20°	964.1	411.3	45	0.440
20°	540.4	684.9	45	0.448
20°	561.0	663.2	45	0.447
20°	422.8	839.6	45	0.465
20°	442.4	815.7	45	0.455
				0.451 Ave.
35°	593.4	413.3	15	0.656
35°	373.0	655.4	15	0.649
35°	357.0	679.4	15	0.654
				0.653 Ave.

DISCUSSION OF RESULTS.

Analysis of the data shows that the efflux is a linear function of the shearing stress, Fig. 1. As the concentration is increased or the temperature lowered the yield value invariably increases. In a few cases the mobility is not constant to within the normal experimental error, but there is no perceptible drift of the values with the shearing stress. Shreds of undissolved cotton will of course give rise to erratic values.

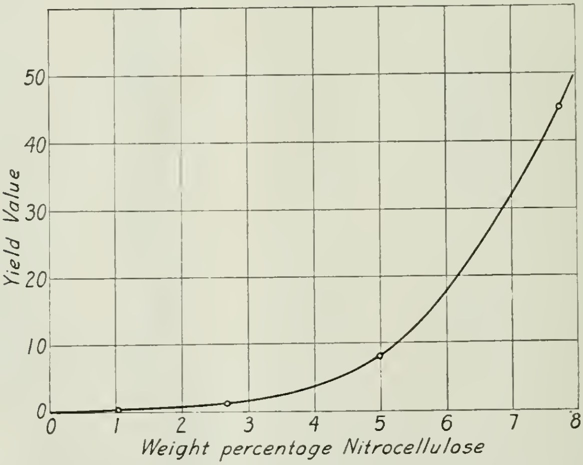
FIG. 3.



The variation of the yield value in dynes per cm.^{2} with the temperature Centigrade, for a 7.708 per cent. dispersion of nitrocellulose in acetone.

On plotting the yield value against the temperature, Fig. 3, for our 7.708 per cent. mixture, there is indicated a sharp transition temperature at 43° C. where the yield value becomes zero, *i.e.*, where the material loses its plastic character and becomes a viscous liquid. The question suggests itself, "Does the colloidal solution become a true solution at the transition temperature?"

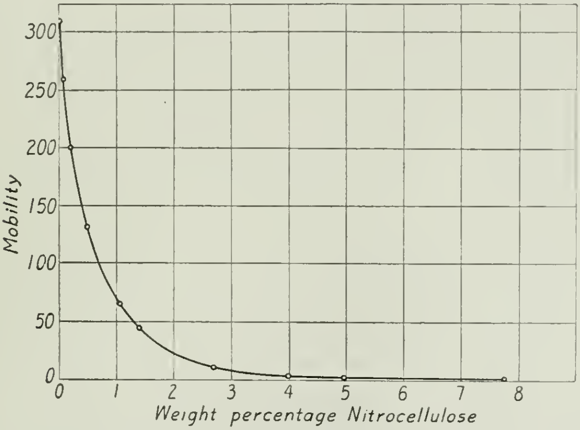
FIG. 4.



Variation of the yield value with the concentration of 20° C. of nitrocellulose dispersed in acetone.

We hope later to investigate the effect upon this transition point of using other varieties of nitrocellulose and other solvents. The yield values for the lower concentrations are too inexact to give us certain information as to the effect of concentration of the nitrocellulose on the transition point; but since all of our solutions have a measurable though very small yield value even at 40°, there is nothing inconsistent with the view that the transition point is independent of the concentration. It is hoped that this transition temperature may serve as a useful criterion, and there is evidence that it may be used in colloidal solutions other than those of nitrocellulose.[11]

FIG. 5.



Variation of the mobility with the weight concentration at 20° C.

The yield value increases rapidly with the concentration, Fig. 4, but not in a linear manner. This is in marked contrast with the behavior of a clay suspension,[12] which is the only case we have to compare with this. A possible relation between the two will be brought out in the next paper.

The mobility of nitrocellulose dispersions is characterized by its extraordinary depression with very small percentages of the solid. Thus a one per cent. solution has a mobility which is only twenty per cent. of the fluidity of the pure solvent, and in an eight per cent. solution the fluidity is lowered to about one-tenth of one per cent. of it original value. This is one of the most noteworthy distinctions between the polar and non-polar type of colloid. The relation between mobility and concentration is by no means linear (Fig. 5), the first additions of nitrocellulose being much more effective than the later ones.

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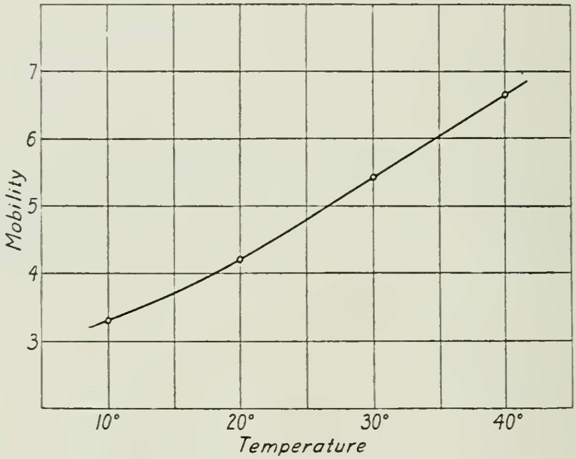
[11] "Fluidity and Plasticity," p. 289.

[12] Do., pp. 220 and 221.

The mobility increases with the temperature in a nearly, although not quite, linear manner (Fig. 6). From 10° to 40° the mobility of a 3.98 per cent. solution increases from 3.33 to 6.64, some 66.6 per cent. Over the same range of temperature acetone increases in fluidity from 279 to 373, or 28.8 per cent. The increase in mobility is therefore only partly due to the increase in the fluidity of the acetone, but it is due to an even greater extent to the solution of the nitrocellulose in the acetone.

FIG. 6.



The variation of the mobility with the temperature Centigrade of a 3.08 per cent. dispersion of nitrocellulose in acetone.

In conclusion, we have found it possible to measure the plasticity of thin-flowing materials in the viscometer. We have found that certain substances of colloidal character, which have hitherto been supposed to have a definite fluidity, do not behave like true liquids as measured in the customary manner. By using a variety of shearing stresses, simple relationships are obtained.

More than 1500 technically trained persons, according to reports to the United States Department of Agriculture, are employed in studying farming problems in the State agricultural experiment stations. In 1921, 400 publications were issued containing results of their work.

A THEORY OF THE STRUCTURE AND POLYMORPHISM OF SILICA.*

BY

ROBERT B. SOSMAN, Ph.D.

Physicist, Geophysical Laboratory, Carnegie Institution of Washington.

INTRODUCTION.

One can nearly always find a few specimens of quartz about a research laboratory, and there never was a museum, however small, that did not have some specimens of "rock crystal." Here, I suspect, is the reason why we now have such a variety of physical data on quartz; everyone who invented a new apparatus or method found quartz a convenient standard substance on which to try out his invention. Silica glass, also, because of its scientific and its industrial interest, has been the subject of many measurements. Not so many data are at hand on the other crystalline forms of silica, but, all told, a good deal is known about their relations to one another.

This body of data furnishes particularly attractive material for the "indoor sport" of theorizing about the structure of matter, since the process of building up a successful combination of hypotheses is the more complex and intriguing, the greater the variety of data to be explained. In the very properly limited space of a journal article I shall attempt only to sketch the outline of what I consider to be a consistent theory, or set of hypotheses, concerning the structure and polymorphism of silica, and to show how these hypotheses explain a few of the better known properties of silica. It need hardly be said that each hypothesis cannot, at the moment, claim any large likelihood of permanence, because new facts, especially facts concerning the arrangement of the atoms in space and the structure of individual atoms, are rapidly being obtained. Nevertheless, if we can find a set of hypotheses which satisfies the large body of existing facts about silica, it may prove to be the permanent basis for a dependable theory which will need to be modified only in minor points.

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* Communicated by Dr. Arthur L. Day, Director of the Geophysical Laboratory and Associate Editor of this Journal. First presented at the general meeting of the American Chemical Society of Birmingham, Alabama, April 5, 1922; also before the Philosophical Society of Washington, November 4, 1922.

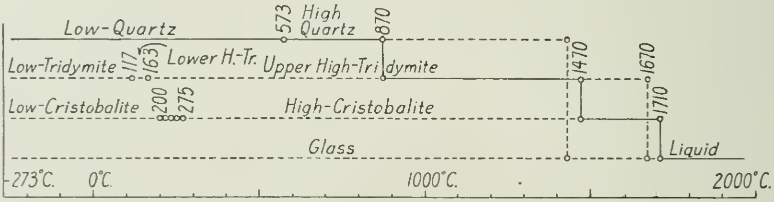
THE FORMS OF SILICA AND THEIR INTERRELATIONS.

At atmospheric temperatures and pressures there exist three distinct crystalline modifications of silica which have been recognized and studied in the laboratory,[1] namely, *quartz, tridymite,* and *cristobalite.* All three undergo enantiotropic inversions at higher temperatures; quartz has one such inversion; cristobalite, one; and tridymite, two, making a total of seven recognized crystalline modifications, to which must be added an eighth modification, the fused or glassy. The mutual relations of these eight are exhibited graphically in Fig. 1.

THE INDIVIDUALITY OF THE SiO_2 ATOM-TRIPLET.

Every chemist believes that there are certain groups of atoms, particularly groups containing carbon, which retain an individuality in the gaseous, liquid, and crystalline states, whether the group be itself a pure substance, or a constituent part of a relatively complex compound. There is much evidence that this is true of the silica atom-triplet, SiO_2. I use "atom-triplet" instead of "molecule," since the word "molecule" has many connotations in which we are not now interested. This individuality of SiO_2 is recognized in our common groupings of chemical facts. In the text-books of chemistry the silicates are recognized as a proper subject for unified treatment, while the sulfates or chlorides are classified according to their metallic constituents. Under atmospheric conditions the silicates are nearly all transparent crystalline solids, insoluble in water and the usual solvents. They melt above a red heat to form viscous liquids of low volatility. Most of them are easily con-

FIG. 1.



Graphic representation of the relations between the forms of silica. (Solid lines represent stable states, dotted lines represent unstable states.)

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[1] See especially Fenner, *Am. J. Sci.*, 36, 331–384, 1913.

verted into glasses, which are strikingly alike in many of their properties.

In an earlier paper[2] summarizing the temperature-composition diagrams of the commoner two- and three-component silicate systems, and commenting on some of their properties, I have emphasized the evidence furnished by those data in favor of the assumption that, in the silicates, SiO_2 acts as a unit. For the present the reader is requested to take that assumption for granted, as there is not space here to enter into a full discussion of this complex and much-argued question of the constitution of the silicates.

Assuming, as the basis of the argument, that the SiO_2 atom-triplet does retain its individuality in the silicates, we may reasonably expect that it will be found as an individual triplet in its pure crystalline forms, as well as in its liquid and vapor states. If this is true of the crystalline forms, it sets off silica as being markedly different from such strongly polar compounds as sodium chloride, for from X-ray studies it is now clear that a crystal of NaCl is a structure built up of Na and Cl atoms, or rather ions, and is a structure within which no definite groupings of atoms are recognizable. In crystalline silica and the silicates, on the contrary, definite triplets of the composition SiO_2 should be distinguishable.

The fact, however, that over a wide range of temperature silica in all its forms is an elastic solid, shows that some force prevents the free movement of each triplet as a whole and holds it in a fixed position in the crystal. The nature of this force is not entirely clear. In some crystalline compounds, no doubt, the process of forming the compound is one and the same with the process of forming the crystal, that is, the compound does not exist in the liquid or gaseous state. In others, the solid state may result entirely from the residual electric or magnetic field of permanent stable molecules. In silica, we shall assume that the solid state is the result of an interlocking or interpenetration of some of the electron orbits of neighboring atom-triplets.

Our ultimate problem, then, is to find the pattern according to which the silicon and oxygen atoms are arranged in space, and to find a manner of interlocking of electron orbits which will account (1) for the formation of the SiO_2 triplet, (2) for its building up into solid substances of several different forms, and (3) for the changes that it undergoes at the inversion points of the forms.

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[2] R. B. Sosman, *J. Ind. Eng. Chem.*, **8**, 985–990, 1916; *Trans. Faraday Soc.*, **12**, 254–263, 1917.

Our most direct information as to the arrangement of the atoms comes from X-ray diffraction, but we have relatively few data of this kind on silica. These will be discussed in the next section, after which the further development of the theory will be based on the polymorphism and physical properties of the forms.

EXISTING DATA ON THE POSITIONS OF THE ATOMS.

The analysis of crystal structure by means of X-rays has not yet been developed to the point where the structure of a complex substance of hexagonal, trigonal, or orthorhombic symmetry can be determined with the completeness and certainty which are possible for a cubic crystal. No atom-pattern, supported by X-ray refraction data, which would exclude the possibility of other atom-patterns, has yet been put forward for any of the modifications of silica. It is still necessary to fall back upon the procedure of theorizing about the shape and dimensions of SiO_2 and to adopt the result which best fits the known properties.

Bragg[3] has measured the angles of reflection of X-rays from the faces of a quartz crystal and has suggested that the data may be explained by means of a threefold hexagonal lattice, namely, three interpenetrating hexagonal lattices derived from each other by equal translations parallel to the axis *c*, together with rotations of 120° about that axis. There would be three SiO_2 atom-triplets to each unit of structure, and each hexagonal lattice would locate the positions of one-third of the triplets. Two independent structures of this kind are possible, the one "right-handed," the other "left-handed" in its direction of rotation. The distance of the silicon atoms from the axis of rotation, and the relative positions of the oxygen atoms with respect to the silicons, remain undefined.

Bragg's structure does not satisfactorily explain all the optical properties of quartz, or its crystallographic growth-forms. The structure suggested by Beckenkamp[4] better satisfies the optical and crystallographic requirements, and at the same time seems to be in agreement with Bragg's X-ray reflections.

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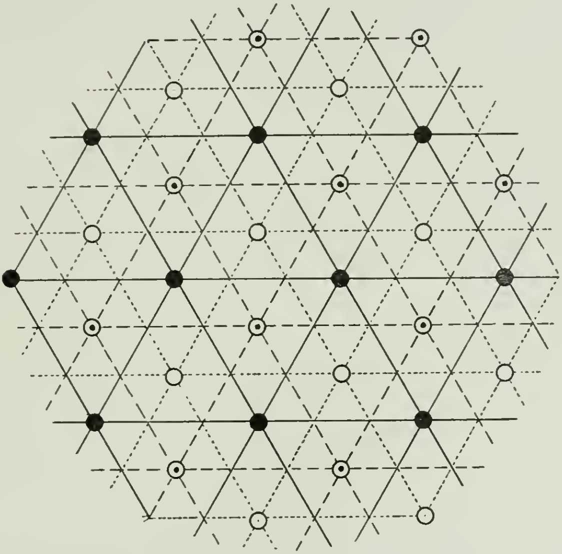
[3] W. H. Bragg and W. L. Bragg, "X-rays and Crystal Structure" (London, 1915) p. 160.

Low-quartz,[5] according to Beckenkamp's structure, contains the *silicon* atoms in a rhombohedral lattice, which is in effect a threefold triangular prismatic lattice derived as shown in Fig. 2. Fig. 2 shows the plan of the structure, the trigonal axis being vertical. The solid circles represent one horizontal layer of silicon atoms; the centred circles, the next horizontal layer above the first; and the open circles, the third horizontal layer. The fourth layer is like the first, and so on. The rotation (which may be considered either right- or left-handed) is about an axis equidistant from the three kinds of circles. Thus far, the structure may be considered to be the same as Bragg's for the silicon

FIG. 2.



Rhombohedral lattice of silicon atoms in low-quartz.

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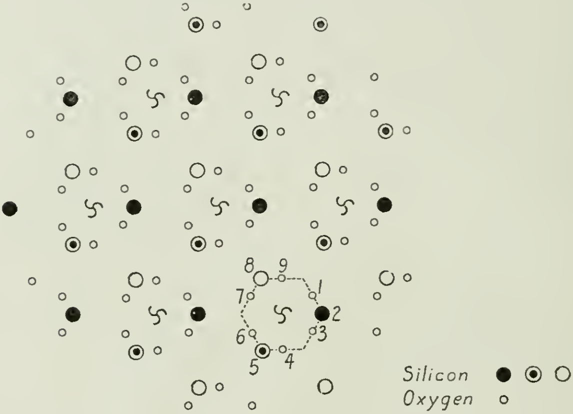
[4] J. Beckenkamp, *Z. anorg. Chem.*, 110, 290–310, 1920.

[5] Divergent usage of α and β has created hopeless confusion in the nomenclature of silica. I have therefore dropped the Greek prefixes entirely, and use the English prefixes "high-" and "low-," as abbreviations, respectively, for "high-temperature-" and "low-temperature-."

atoms, with the distance of the silicons from the rotation-axis so defined that the right- and left-handed rotations are indistinguishable.

The positions of the oxygen atoms in the structure, however, depend upon whether the crystal is right-handed or left-handed. In right-handed low-quartz, the oxygens (and silicons) are situated as shown in the plan in Fig. 3. The lowest layer of atoms is numbered 1, the next above 2, and so on up to 9, number 10 being directly above number 1. Numbers 1 and 3, 4 and 6, and 7 and 9, respectively, are the pairs of oxygens associated with silicon atoms which are numbered 2, 5, and 8. The series of 9 atoms (3 SiO_2 triplets) thus forms a helix rotating upward to the right. The vertical planes in which the oxygen atoms lie are evident from the plan; viewed horizontally, the positions of the oxygens may be defined as lying upon the edges of the hexagonal prism containing silicon atoms of corresponding planes, that is, the first, fourth, seventh, etc., silicon planes.

FIG. 3.



Plan of the structure of right-handed low-quartz. The same silicon atoms are shown as in Fig. 2.

On tridymite and cristobalite we have no X-ray data from which any conclusions as to the relative positions of the atoms can be drawn.

Before proceeding with the development of a theory which will link up the Bragg-Beckenkamp structure of low-quartz with structures and mechanisms which will explain the relations of all the forms, it will be necessary to devote a few paragraphs to the general subject of polymorphism, with special reference to silica.

POLYMORPHISM.

The term "polymorphism" as currently defined and used applies only to the crystalline state. It is best defined as "that quality of a crystalline substance, having a definite chemical composition, which permits it to appear in modifications having different axial ratios or belonging to different classes of symmetry; changes which are relatively small and at the same time continuous, due to changes of temperature and pressure, are excluded.[6]

Hypotheses as to the cause of polymorphism have generally lumped together all its manifestations and tried to explain them by a single cause. The actual phenomena, however, show wide variations, which may well be traced to different causes. For example, two strongly contrasted types of polymorphism occur in silica.

There is, first, the "sluggish" type of inversion which occurs among the three modifications: Quartz, tridymite, and cristobalite. All three exist at atmospheric temperature and pressure, although only one, quartz, can be stable under those conditions. Nevertheless, the other two are very persistent and are not difficult to obtain experimentally. The principal feature of the inversions from one of these forms to another is their slowness, several hours usually being required for complete transformation, and at certain temperatures and in certain directions the presence of a solution or melt in contact with the silica is necessary before the change will occur at all.

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[6] The Standard Dictionary (1913 revision, 1920 reprint) defines polymorphism as ".... the ability of certain substances to crystallize with different axial ratios without change of chemical composition." This would exclude an isometric substance which remained isometric through an inversion, for its axial ratio has invariably the value 1. It might also experimentally exclude a non-isometric substance, if one were to be found whose axial ratio did not change measurably through an inversion point. (This was at one time thought to be true of high-quartz and low-quartz.) Such modifications are, however, of different symmetry, so that the second criterion in the definition would apply.

The second type of inversion in silica is the "high-low" or "prompt-reversible" type, occurring between the high-temperature and low-temperature forms of quartz, tridymite, and cristobalite. These inversions occur promptly the moment the proper temperature is reached, although it should be noted that this temperature may be different according to whether the temperature is rising or falling; that is, they show a temperature-hysteresis. But, outside of this hysteresis range, the high-form is never found at a lower temperature, nor is the low-form found at a higher temperature. As pointed out by White,[7] the phenomena suggest some change which is common to all the three modifications, yet is affected by the transformation from one modification to another.

The hypotheses which have been advanced to account for polymorphism may be roughly grouped as (1) molecular, (2) structural, (3) atomic.

The molecular type of hypothesis assumes the existence of distinct molecules in the crystalline state, just as in the gaseous and liquid states. It has been most elaborately developed by Smits.[8] Having first shown experimentally that a dynamic chemical equilibrium between different kinds of molecules very probably exists in the liquid and crystalline states of certain substances, Smits' theory goes on to postulate such an equilibrium in every phase of every substance which exhibits polymorphism, and to apply thereto the well-known principles of the phase rule of Gibbs and Roozeboom.

The "structural" hypotheses assume that polymorphous forms of a substance differ simply in the arrangement of their constituent parts in the crystal lattice, whether those parts be molecules, atom-groups, or atoms (Bravais, 1851). Different orientation of the parts, without change of the arrangement in space of their geometrical centres, is also suggested as a variant of this type of hypothesis.[9]

The "atomic" type of hypothesis assumes that the polymorphous change is due to a change of form of some or all of the *atoms* of the substance, without necessarily any change in their arrangement or orientation. The change may be in the positions or orbits of the outside or planetary electrons, or it may be in the atomic nucleus itself.[10]

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[7] W. P. White, *Am. J. Sci.*, **47**, 31, 1919.

[8] A. Smits, *Die Theorie der Allotropie*, Leipzig, 1921.

[9] P. W. Bridgman, *Proc. Am. Acad.*, **52**, 91–187, 1916.

Now it need hardly be said that all these types of polymorphism may actually exist, one in one substance, one in another; or that there may be a real gradation from one type of polymorphism to another.[11] The inversion of benzil-ortho-carbonic acid at 65.7° might be taken as an example of polymorphism which is clearly molecular. The inversion of pure iron at 770° may be best explained as mainly an atomic inversion.[10] To anticipate the conclusions of subsequent sections of this article, the inversions of silica are best explained as partly structural and partly atomic, the sluggish type in silica depending upon a fundamental rearrangement of silicon and oxygen atoms, while the prompt-reversible type goes deeper into the atom but involves also a subordinate change in the relative positions of atoms.

In all this we must bear in mind what constitutes a real hypothesis. One of the most important objections to Smits' theory is the very facility with which it explains all the phenomena. There has been an uneasy feeling among some of those who have followed its development that the theory is capable of explaining not only all existing data on polymorphism, but any that can possibly be discovered. Now a theory which is capable of explaining all imaginable data in its field is, conversely, incapable of predicting any one experimental fact to the exclusion of any other; or, in the pragmatic philosophy, it is not a theory at all, but a form of words. It has happened more than once in the history of science that two formulas which sounded very different, but whose corollaries were experimentally indistinguishable, have led to needlessly long and bitter polemics. Hence it will be well to devote our closest scrutiny to what follows from a theory, rather than to the plausibility and general attractiveness of the formulation itself.

Among the dozens of clues which might give a hint as to the explanation of the polymorphism of silica, the following are particularly suggestive: (1) The coefficients of thermal expansion of the three high-forms are very small, in which they agree also with fused silica; (2) the high-low inversion temperatures are inversely proportional to the specific volumes of the three low-forms. Now a mechanically compact and stable atom-triplet, capable of taking up within itself most of the thermal vibration due to rising temperature, and so constructed that it can be used as a building unit in three different ways to make three space lattices of atoms, would account for the three high-temperature forms; then, if within each of these structures we can find an atomic binding mechanism common to all three, which mechanism is balanced against a force of thermal agitation tending to separate certain atoms in the structure, we can account for the high-low inversions and their dependence upon volume. At the same time, various properties of liquid, glassy, and colloidal silica suggest a thread or chain structure. The next step is to combine these various desiderata into a consistent whole.

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[10] R. B. Sosman, *J. Wash. Acad. Sci.*, 7, 62–67, 1917.

[11] F. Rinne, *N. Jahrb. Min., etc.*, 1916, II, 96.

STRUCTURE OF THE ATOM-TRIPLET.

All lines of evidence now indicate that an atom consists of a positive nucleus surrounded by electrons, whose number equals the ordinal number of the element in the Periodic System. The silicon atom consists of a nucleus with positive charge 14, surrounded by 14 non-nuclear electrons. The oxygen atom has a nucleus with positive charge 8, surrounded by 8 non-nuclear electrons.

The electrons are distributed as follows: In each atom there is an inner pair. The remaining 6 electrons of oxygen then form an outer group, while the remaining 12 of silicon form first a group of 8, and outside of that a group of 4. The tendency in both silicon and oxygen is toward the completion about each atom of a stable external octet, such as characterizes both neon and argon, the inert elements next in order of complexity above oxygen and silicon. This tendency causes the combination of silicon and oxygen to form SiO_2.

At this point theories of the structure of compounds begin to diverge. According to the Lewis-Langmuir theory,[12] the electrons occupy relatively fixed positions in the atom. The formation of octets, just referred to, is accomplished either by the transfer of electrons from one atom to another, or by the sharing of electrons between atoms.

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[12] In the development of the theory of silica I have used the Bohr revolving-electron type of atom. But since the Lewis-Langmuir fixed-electron atom (*J. Am. Chem. Soc.*, 41, 868–934, 1919) is more familiar to chemists, the structure of SiO_2 will be expressed also in terms of that atom-type. That part of the theory of silica which is concerned with the structure of the triplet, and its building up into the solid modifications, would remain the same whichever type of atom be assumed.

My present hypothesis assumes that the silicon atom shares one pair of electrons with each oxygen, and the oxygens share a pair of electrons between them. At the same time the silicon shares one pair of electrons with each of two neighboring silicons.

FIG. 4.

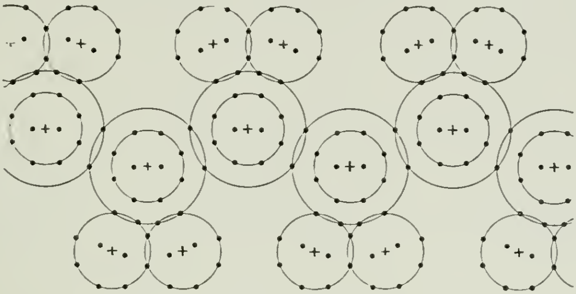
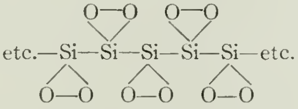


Diagram to illustrate the grouping and sharing of electrons in the silica thread (but not their positions in space).

The result is a *silica thread* built up of SiO_2 atom-triplets as the fundamental building unit. It may be crudely represented in a plane by means of the familiar valence bonds, thus:



$$\begin{array}{c} \mathrm{O{-}O}\qquad\mathrm{O{-}O} \\ \text{etc.}{-}\mathrm{Si}{-}\mathrm{Si}{-}\mathrm{Si}{-}\mathrm{Si}{-}\mathrm{Si}{-}\text{etc.} \\ \mathrm{O{-}O}\qquad\mathrm{O{-}O}\qquad\mathrm{O{-}O} \end{array}$$

or by some such representation as that of Fig. 4. This figure emphasizes mainly the grouping and sharing ideas, without attempting to represent the distribution of electrons in space. The orientation of the oxygen pairs is different in the different modifications of silica, as will appear below.

In terms of Bohr's revolving-electron quantum theory of atomic structure,[13] which now seems destined to replace the fixed-electron theories such as those of Lewis and Langmuir, the structure may be described as follows:

Around the silicon nucleus revolve two electrons in "uniquantous" (German *einquantige*) orbits. The stable structure of 10 electrons which characterizes the neon atom and constitutes the inner foundation of the silicon atom consists of this pair and two groups of 4 electrons in "biquantous" orbits, of which 4 are elliptical and 4 approximately circular (designated as orbits of types 2_1 and 2_2). These two groups of 4 biquantous orbits correspond numerically to the octet of Langmuir, but the octet is no longer considered as a "shell" of electrons. The remaining 4 electrons revolve in triquantous (type 3_1) orbits.

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[13] N. Bohr, *Zeitschr. Physik*, 9, 1–67, 1922.

Similarly, in the oxygen atom there is an inner pair, a group of 4 electrons in orbits of the type 2_1 and 2 electrons in orbits of the type 2_2.

When these two atoms, silicon and oxygen, react together, the tendency is for each to complete a stable structure of electron orbits. The oxygen atom builds up a neon structure by taking 2 electrons from other atoms into orbits of type 2_2 which during a part of their course probably penetrate even into the region of the inner electron pair near the oxygen nucleus; in the same way the silicon atom tends toward the argon structure by taking on 4 foreign electrons in orbits of type 3_2 which penetrate to the neighborhood of the silicon nucleus.

The present hypothesis supposes that 2 of the electrons added to the silicon come from neighboring silicons, and the other 2 from the 2 oxygens; the 2 electrons added to each oxygen are drawn, one from the silicon and the other from the second oxygen. The formal representation of this bonding used with the Lewis-Langmuir theory may be equally well used, as a first approximation, with the Bohr theory.[14]

The resulting three atom-structures (one silicon and two oxygens) are roughly tetrahedral, because of the grouping of electrons of the "octet" in pairs, and the three are closely assembled into an atom-triplet which is roughly trigonal. The sketch in Fig. 5 will give an idea of its form, if three interlocking solar systems can be said to have a form.

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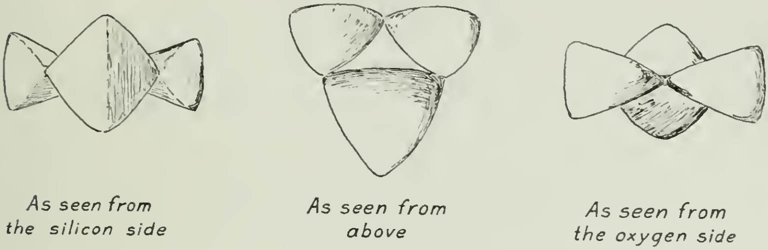
[14] See also footnote 12. Since this paper was presented, an article by Huggins on "The Crystal Structure of Quartz" has been published (*Phys. Rev.*, 19, 363–368, 1922). This article presents no new experimental data, but proposes a very reasonable hypothesis of the structure, based on the Lewis-Langmuir hypotheses. It supposes that all the linkages between atoms in low-quartz are primary valence linkages between silicon and oxygen, making the crystal a continuous "molecule." The hypothesis offers no explanation, however, of any of the numerous other modifications of silica, or of the phenomena of the inversions; some of the arguments in its favor employed by its author in describing the structure of low-quartz would apply equally well to any of the other modifications, and all of them would apply equally well to high-quartz.

STRUCTURES OF THE VARIOUS MODIFICATIONS.

Liquid and Glassy Silica.—As already remarked, the present hypothesis supposes the silica atom-triplets to be joined up into threads. These threads form in the liquid state and their formation may begin even in the vapor. In the liquid they are in a constant state of vibration and movement, with the oxygen pairs in haphazard and probably varying orientation relative to the thread. A drop of silica glass in the neighborhood of 1700–1800° would resemble a mass of wriggling worms. The threads themselves not improbably have a helical twist.

FIG. 5.



Sketch to aid in visualizing the shape of the SiO_2 atom-triplet.

If the temperature is rapidly lowered the threads become less and less active, until at last the mass becomes like a compressed pad of wires, and we have " solid " silica glass. An intricately tangled mass of wires has some of the properties of a solid, even though the individual wires are flexible.

The drawing out of a lump of such glass into a rod might naturally be expected to disturb the haphazard arrangement of the threads and give some of them a prevailing orientation parallel to the rod. This would explain the difference in expansion parallel and perpendicular to the axis in silica rods or tubes,[15] and the variation in expansion between different samples, indicated by some experiments. It perhaps will also aid in explaining the evidences of ribbon-like crystallinity in silica glass rods, observed by Rayleigh.[16] The thread hypothesis is also in accord with the familiar habit of amorphous silica of condensing in fine fluffy or lint-like forms. It has even been obtained from the electric furnace in microscopically fibrous massive form, a *fibrous glass,* which is wholly non-crystalline to an X-ray exposure of ordinary length,[17] though showing traces of a structure under longer exposures.

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[15] Callendar, *Phil. Mag.*, **23**, 998–1000, 1912. The difference is usually not so great as the first measurements indicated.

Cristobalite.—Suppose the cold silica glass reheated to a temperature in the vicinity of 1600°, which is below the melting temperature of cristobalite. The threads resume their active movements, but we must now take account of certain constraints upon these movements. The larger size of the silicon atom as compared with the oxygen distorts the latter so that there is a residual force at the " outside edge " of each oxygen which tends to hold oxygens together whenever they accidentally approach one another, perhaps because electron orbits from two neighboring oxygens actually interlock during such an approach. The result is a gradual straightening out of the threads and their building up into a crystalline structure of external cubic symmetry, the modification known as *high-cristobalite.* The specific volume and the expansion coefficient remain practically the same as for silica glass.

The silica threads are now assumed to lie parallel to a cube diagonal, that is, perpendicular to an octahedral face. Their relation to the cube will appear from the following considerations. Suppose the silicon atoms arranged in some variety of cubic lattice. Then imagine this structure turned up on one corner so that the octahedral normal is vertical. It may now be considered a rhombohedral lattice. For example, if the cubic lattice be a face-centred cube, its axial ratio considered as rhombohedral would be $a : c = 1 : \sqrt{6}$ or $1 : 2.4495$. The vertical (trigonal) axis is assumed to be the axis of the silica thread, and the silicon atoms will be found to be arranged around it in helical fashion but in a helix which is considerably more drawn out lengthwise than in quartz. The oxygen pairs tend to orient themselves in the octahedral (now horizontal) planes, perpendicular to the axes of the threads. The direction of rotation of the helix, whether right- or left-handed, is purely a matter of chance and the two kinds are probably present in equal amounts. The structure will be further discussed when we come to the high-low inversions.

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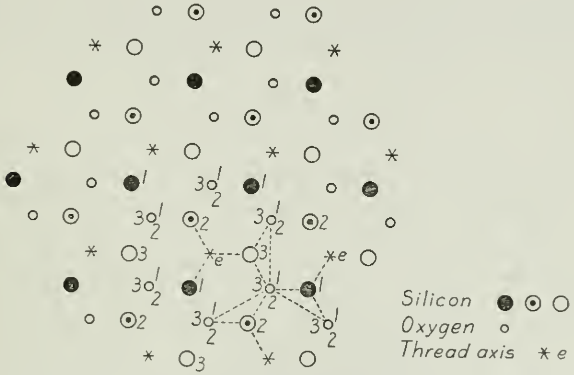
[16] *Proc. Roy. Soc.,* London, A **98**, 284–296, 1920.

[17] Photographs by Dr. E. W. Posnjak of this Laboratory.

Tridymite.—When the temperature falls below 1470° the diminished thermal agitation permits of a more stable configuration, namely, that of *high-tridymite.* The structure is hexagonal in external symmetry. The silica threads are parallel to the hexagonal axis, but are shrunken longitudinally, bringing the axial ratio for the silicon lattice down to about 1 : 1.7. The oxygens now assume definite positions throughout the structure, each pair lying in a plane perpendicular to the thread direction, and the lateral distance between the threads increases.

FIG. 6.



Plan of the structure of high-tridymite. The same silicon atoms are shown as in Figs. 2 and 3.

A plan of the structure is shown in Fig. 6. Successive planes of atoms are numbered 1, 2, and 3. It will be found that if the vertical axis *e,* along which the silicons are joined together, be taken as a centre of reference (which we might call an "electron-well" since the interlocking electron orbits between the silicons of a thread all cross this axis) the oxygen atoms occupy 6 "wells" all equally distant from the centre; all of these contain oxygens equally spaced along the vertical axis.[18]

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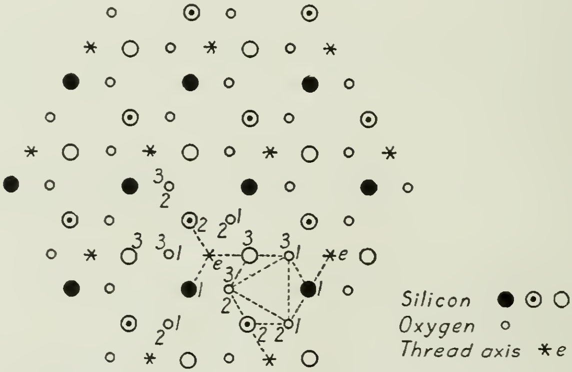
[18] The structure is not in all respects satisfactory, since it may be necessary to assume twinning in order to account for the dihexagonal symmetry of high-tridymite. Beckenkamp also finds this necessary with his theoretical structure for tridymite, based on that of low-quartz. An untwinned structure would be better.

Quartz.—Further lowering of the temperature to 870° brings about still another rearrangement, producing the modification known as *high-quartz*. The structure is trigonal in external symmetry. The silica thread persists as in cristobalite and tridymite, but the silicon atoms have again been brought somewhat nearer together along the hexagonal axis. The essential change is in the position of the oxygens. These no longer occupy 6 wells around each electron-well, but instead occupy 3 close to the electron-well and another 3 farther away, and are arranged in vertical pairs, as is evident from the plan in Fig. 7, in which the successive planes of atoms are numbered 1, 2, and 3. The structure is rotatory, being either right- or left-handed.

FIG. 7.



Plan of the structure of high-quartz. The same silicon atoms are shown as in Figs. 2, 3, and 6.

General Remarks.—The foregoing structures for high-cristobalite, high-tridymite, and high-quartz agree well with the known interrelations of the forms, and the high-quartz structure fits on to that of low-quartz, as will be shown presently. For example, silica glass always crystallizes first to cristobalite, even in the tridymite and quartz ranges. Quartz likewise inverts directly to cristobalite even in the tridymite range, sometimes apparently passing through a stage of fusion. This is because the shaking down of quartz threads into amorphous threads by thermal agitation at high temperatures makes the formation of the relativity incomplete cristobalite structure (see page 760 following) a more easily attainable result than the rearrangement of the whole oxygen lattice to form tridymite; the tridymite reconstruction requires time or the aid of a solvent. Again, right-handed high-quartz remains right-handed on cooling; although it sometimes becomes twinned, the twinning is always of the Dauphiné type, in which all the individual parts are right-handed or all left-handed, and never of the Brazil type, which is alternately right and left.[19] The cause of this is obviously the connection together of the two oxygens of the triplet; to make a right-handed crystal into a left it is necessary to disconnect the oxygens and move them around to the other side, which practically means disintegrating the quartz by means of a solvent, while the other type of twinning can be accomplished by merely rotating a part of the threads as units.

THE HIGH-LOW INVERSIONS.

As we have just seen, the maintenance of the crystalline structure of the forms of silica depends upon two constraints: First, the connection of the silicon atoms into threads; second, the attraction between the outer ends of oxygen atoms belonging to different atom-triplets or different threads. These constraints are similar in character in all three modifications.

The mechanism of the high-low inversion is likewise similar in all three modifications. The phenomena in quartz are the best known and furnish the most valuable clue to the atomic mechanism. Most, if not all, of the properties of quartz begin to change noticeably at a temperature considerably below the inversion, and progress according to a logarithmic law up to 573° where there is a sudden jump to an entirely different curve of change. As I have pointed out elsewhere,[20] this form of curve is duplicated exactly by the curve showing the relation between the angular velocity and the moment of the forces on two coaxial cylinders rotating in water. There is a limiting value of speed below which the moment is proportional to the speed, and above which the square of the speed enters, with a discontinuity separating the two states of motion.

An equally instructive analogy is found in the state of oscillation of two coupled oscillatory electric circuits, one of which is supplied by an electron tube.[21] In this case the curve of current against the natural frequency of the secondary circuit, when the frequency is varied continuously, not only jumps suddenly at a certain point, but jumps back at a *different* point when the conditions of change are reversed. In showing this "oscillation hysteresis" the system duplicates exactly the behavior not only of quartz, but of all the high-low inversions of silica, since all show a definite "temperature hysteresis" in the inversion phenomena according as the temperature is rising or falling. This behavior is also duplicated by high-low inversions in iron and other substances.

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[19] Beckenkamp, *op. cit.*

[20] *Amer. J. Sci.*, **37**, 19, 1914; *N. Jahrb. Min., etc.*, Beil. Bd. **40**, 139, 1915.

[21] Van der Pol, On oscillation hysteresis in a triode generator with two degrees of freedom, *Phil. Mag.*, **43**, 700–719, 1922.

Evidently some subsidiary part of the structure (triplet, atom, nucleus, or electron) is in a state of motion which varies with the temperature, but which influences the motion of some other subsidiary part in such a way that the secondary motion changes suddenly from one state to another. This performance probably does not take place mainly or entirely within the triplet, else all the forms of silica would have an inversion at about the same temperature. On the contrary, the inversion temperature is roughly inversely proportional to the volume of the low-form.

I have therefore assumed that the high-low inversion affects chiefly the "outside" linkage between oxygens which, under the present theory, is one of the two constraints holding the crystal together. We may then suppose the inversion (with rising temperature) to consist (1) in an increase of amplitude of the thermal vibration of a pair of oxygen atoms, which (2) influences the manner of revolution of a pair of electrons, with the result that (3) a relatively constant attraction between the two oxygens becomes balanced by an increasing repulsion between the two orbits in question. At a certain temperature the existing structure becomes unstable and the oxygens move suddenly to a new position characteristic of the high-form. Until we know more about the form and distribution of the 32 electron orbits which we assume to exist in each triplet, it will not be possible to specify more exactly the character of the change in the orbital motions. Perhaps it consists in the production of rotational vibrations of the plane orbits of the inner pair, which vibrations become actual rotations of those planes at the inversion point. This would be a possible electron mechanism to explain Ashworth's theory of the high-low inversion in iron.[22] Experiments on the effect of an A. C. field upon the magnetic properties of quartz through the inversion point might throw light on this question.

Quartz.—In the structure of low-quartz (see p. 746) the plane of the silicon and the two oxygen atoms of a triplet stands at an angle to the hexagonal axis, bringing the oxygens of successive triplets near each other in what we might call "external pairs," to distinguish them from the "internal pairs" of the SiO_2 triplets themselves. Three such external pairs complete the circuit of the helix. As the temperature rises the increasing amplitude of vibration of the oxygen atoms finally brings about, at 573° C., a sudden change in the mode of revolution of certain electrons associated with the two atoms. The atoms are pushed apart into a new position in which they form vertical pairs, all equally distant from the "backbone" or "electron-well" of the thread of SiO_2 triplets. This simple change of shape of the SiO_2 triplet, which is all that the movement amounts to externally if the electrons are not considered, gives us the high-quartz structure already described.

Tridymite.—In the tridymite structure the oxygens are farther apart than in quartz, and the mutual influence of their electron orbits is less. A smaller increase of temperature (to 117° C.) is therefore sufficient to break up the interlocking which is characteristic of low-tridymite and convert it into the type which is characteristic of the high-form. The high-form itself, however, has two modifications, an upper and a lower, with an inversion at 163°. This 163° change gives a very small heat-effect, and is probably only a final step in completion of a principal change which occurred at 117°. An explanation for it may be found in the fact that from the high-tridymite structure previously described there may be derived *two* kinds of association of oxygen atoms, since the radial distance between oxygens is nearly but not quite the same as their axial distance, while in quartz the oxygens are definitely associated in pairs. But not enough is known of the symmetry and other properties of low-tridymite, or of the differences between the upper and lower high-tridymites, to warrant the construction of models for the lower forms.

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[22] J. R. Ashworth, The theory of the intrinsic field of a magnet and the relation of its magnetic to its characteristic electric and thermal properties, *Phil. Mag.*, 43, 401–419, 1922.

Cristobalite.—Cristobalite exhibits the unusual property, which Fenner was the first to observe in silica, of a variable inversion temperature. The higher the temperature at which the cristobalite was formed, the higher is its high-low inversion point. The explanation of this property evidently calls for some kind of structure which changes at high temperatures but which is preserved at lower temperatures and is not affected by the inversion. It can be accounted for by assuming that the structure is incomplete as regards the oxygen atoms, only a part of the triplets being held in relatively fixed positions while the others still vibrate or rotate about the axis of the silica thread. Rapid cooling to the neighborhood of 200–300° then preserves this mixed structure.

In low-cristobalite the average distance of oxygen atoms is intermediate between that in quartz and that in tridymite. Its range of inversion temperatures is also intermediate (200–275°). But according to the above hypothesis of its structure, the arrangement of oxygens is not complete, some being in haphazard positions just as they were in the glass from which the cristobalite was derived. Accordingly, the oxygen pairs are variously spaced and not all of them will invert at the same temperature; the inversion curve will be drawn out and rounded off, as has been found experimentally by several investigators. The "inversion-temperature" determined by a time-temperature curve (the method used by Fenner) is therefore only a mean value, or a temperature near which the most of the pairs invert. It will readily be seen that as the proportion of haphazard oxygen-pairs is varied by heating the cristobalite at different high temperatures, the mean inversion-temperature will also vary. The phenomenon is rare among polymorphic substances because few are so slow as silica in attaining structural equilibrium.[23]

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[23] The structure proposed for high-cristobalite is perhaps the least satisfactory part of the theory. I know of no facts in opposition to it, but it involves an unusual assumption, namely, that it is possible to have a crystalline substance in which not all the atoms are in geometrically defined positions. With apologies to specialists in phase rule and thermodynamics, it might be crudely called a "solid solution of a glass in a crystal." If later X-ray work on cristobalite should prove this impossible, then some other mixed structure must be found which changes at high temperatures but is preserved by rapid cooling and is unaffected by the inversion.

Silica Glass.—The solid character of silica glass is due primarily to the existence of long silica threads and their entanglement, and only secondarily to the interconnection of oxygen atoms. Externally paired oxygens can doubtless be found, but their distances apart vary continuously over a wide range of values. Accordingly, the high-low inversions in those pairs are scattered over a range of temperatures and no marked effect is discernible at any one temperature.

Chalcedony.—Specimens of chalcedony examined by Hull gave an X-ray pattern which is identical with that of quartz.[24] But Fenner could find no evidence of the 573° quartz inversion in his specimens of chalcedony, and the fact that his material changed partly into quartz and tridymite below 870° also indicated that it could not be the same substance as quartz. If we assume that chalcedony is a submicroscopic fibrous mixture of quartz-threads and amorphous-threads the facts are accounted for. There might be an insufficient number of similarly interconnected oxygen-pairs in such a mixture to give a sharp inversion point, and the amorphous-threads would not give any pattern on the X-ray plate, although the quartz-threads would, if grouped in units having a diameter of the order of magnitude of colloid particles. Other facts, such as ease of conversion to cristobalite, are also consistently explained. Slightly different arrangements of the quartz-thread groups without actually interconnecting them, together with the presence of variable small amounts of water between the threads, will probably suffice to account for the variable optical properties which have led mineralogists to distinguish between certain varieties known as quartzine, lutecite, etc.

At the same time it is important to remark that the name "chalcedony" may cover a number of distinct substances, and comparative results on the *same specimen* are much needed.

EXTENSION TO SILICATE SYSTEMS.

If the foregoing hypotheses are true as regards the self-containedness of the SiO_2 triplet, its association into threads, its threefold upbuilding into crystalline modifications, and the intimate nature of its high-low inversions, then they should be capable of extension into the theory of systems of which silica is a component. There is not space here to take up such an extension in any detail, and I shall indicate only a few scattered applications. In the system $SiO_2 : H_2O$ the thread hypothesis seems capable of accounting for some of the properties of colloidal silica. A stiff silica gel, for instance, may be pictured as something like a wad of cotton saturated with water.

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[24] Washburn and Navias, *Proc. Nat. Acad. Sci.*, 8, 1–5, 1922.

The polymorphism of the silicates offers many interesting suggestions. The 1:1 aluminum silicate, Al_2SiO_5 or $Al_2O_3.SiO_2$, shows the following parallel with silica in density and stability:

	SiO_2	$Al_2O_3 . SiO_2$
Densest form, unstable at high temperatures:	Quartz	Kyanite
Stable high-temperature form, intermediate in density:	Cristobalite	Sillimanite
Lightest form, nearly same density as stable form:	Tridymite	Andalusite

The threefold sluggish-type polymorphism of silica is again duplicated in the three forms of the potash feldspar ($KAlSi_3O_8$) and possibly in soda feldspar ($NaAlSi_3O_8$), magnesium metasilicate ($MgSiO_3$), and other silicates. The negative expansion coefficient of high-quartz appears in two of the axes of the highly siliceous soda and potash feldspars (Fizeau.) The high-low inversion curve of quartz is duplicated in detail by a similar high-low inversion in leucite at a slightly higher temperature. And so on. These are scattered examples among the silicates of phenomena whose explanation must take into account the theory of polymorphism of silica itself.

ANALOGIES WITH OTHER ELEMENTS OF GROUP IV.

The foregoing hypotheses have been based in part upon an atomic structure for silicon containing 4 "outside" electrons, or 4 electrons in a group having orbits of the highest quantum number. We must expect then that other elements having a similar external structure will show similar chemical phenomena.

There are some suggestive analogies between the properties of silica and those of the dioxides of the other tetravalent elements close to silicon in the Periodic System. The four oxides, TiO_2, GeO_2, ZrO_2, and SnO_2, are all solid oxides of high melting point, which combine with water to form colloidal hydrates and with basic oxides to form solid compounds (titanates, germanates, zirconates, stannates) showing many resemblances to the silicates. The analogies in their polymorphism are equally suggestive. TiO_2, the best known of the four, exists in three polymorphic forms, each of which has a temperature-range of stability, like the three forms of SiO_2. SnO_2, likewise, exists in three forms,[25] which appear to be isotrimorphous with the forms of TiO_2, but whose properties have not been determined with certainty. Much less is known of ZrO_2, of which two forms are on record; while GeO_2 has scarcely been studied at all and the desired data are wholly lacking. High-low inversions occur in all three forms of TiO_2 and in the cassiterite form of SnO_2, as is revealed by specific heat determinations.[26] Further search for such inversions in all the dioxides mentioned should yield results of interest.

SUMMARY.

There exists a wide variety of experimental data on the forms of silica, and particularly on quartz, which have never been assembled and explained on the basis of a single consistent set of hypotheses as to the ultimate structure of this substance. This paper attempts to provide such a set of hypotheses, based upon the general knowledge already gained concerning the structure of matter in general and silica in particular.

It is believed that the silica atom-triplet maintains a certain degree of individuality in its amorphous and crystalline states as well as in its compounds, and the freedom of its oxygen atoms to change their positions with respect to the silicons is restricted. The triplets are assumed to assemble into chains or threads in the liquid and glassy states, and a thread structure persists in the crystalline states. The three principal crystalline modifications (cristobalite, tridymite, quartz) are built up by combining the threaded triplets in three different ways, the connection between threads being through the oxygen atoms. The high-low $(\alpha - \beta)$ inversions in all the forms are thought to be due to the same underlying mechanism, namely, a change in the state of motion of certain electron orbits, resulting from increased thermal vibra-

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[25] Wunder, *J. prakt. Chem.*, 2, 206–212, 1870.

[26] Lashchenko, *Bull. Inst. Polyt. Don*, 2, 8–46, 1913.

tion of the atoms, whereby the shape of the silica triplet and the relative positions of the two oxygen atoms are suddenly altered.

The theory as a whole gives a satisfactory explanation for many phenomena of silica not discussed in this paper, such as the minimum in the temperature-volume curve of silica glass, the relations between the specific heats of the crystalline forms, the effect of surface and of twinning on the conversion of quartz into cristobalite, the fact that natural quartz formed at a high temperature is always homogeneous, while low-temperature vein-quartz is right- and left-twinned, etc. Further, many phenomena not yet tested experimentally are predictable from the theory. I hope to take up these matters in more detail in a book on the properties of silica, which is now in preparation.

CORRECTION.

THE APPLICATION OF THERMODYNAMICS TO HETEROGENEOUS EQUILIBRIA.

BY

GEORGE W. MOREY,

Physical Chemist, Geophysical Laboratory, Washington, D.C.

(JOURNAL OF THE FRANKLIN INSTITUTE, October, 1922, page 425.)

Page 455, line 8, parenthesis in equation should read $(1-x)$.

Page 463, last 4 lines should be omitted, beginning with "Fig. 7 shows" etc.

Page 480, 4th line from bottom, equation should read:

$$\frac{\delta\mu}{\delta T} = -\frac{\delta S}{\delta m_1} = -\bar{s}_1$$

Determination of the External Magnetic Field of the Sun from the Structure of the Corona of the Sun and the Constants of the Aurora Borealis. CARL STORMER. (*Comptes Rendus*, June 6, 1922.)—The author makes use of results coming from his expedition to Bossekop in 1913 to calculate the strength of the external magnetic field of the sun. At its equatorial surface this amounts to $.6 \times 10^{-7}$ gausses, while at its polar surface the value is twice as much. These are of the same order of magnitude as those obtained by Deslandres in 1911, but they are notably smaller than the strength of field found, on the basis of the Zeeman effect, by Hale for regions within the solar atmosphere.

The assumption is made that the same corpuscles are in evidence both in the auroral streamers and in the aurora borealis.

G. F. S.

THE HEAVISIDE EXPANSION THEOREM.*

BY

LOUIS COHEN, Ph.D.
Consulting Engineer, Signal Corps, U.S.A.

HEAVISIDE formulated a theorem, known as his " Expansion Theorem,"[1] which is of great utility in the solution of many electrical problems. By the aid of this theorem the current distribution in any network of circuits, the steady state, as well as the transient state, is readily obtained. The theorem is of course of greatest importance in the determination of transient effects which by the usual methods is at best a laborious process, the difficulties increasing as the number of degrees of freedom of the system increases. The reason, perhaps, that this important theorem is not as widely known and as extensively used as its merits deserve may be due to the fact that the derivation of it as given by Heaviside offers difficulties for the engineer and physicist to follow, and its importance was therefore not fully appreciated.

The following simple derivation of the theorem making use of the Heaviside expansion methods will, it is hoped, create a greater interest in the application of this theorem to the solution of electrical problems. The derivation of the theorem is worked out for two cases; a constant electromotive force, and a sinusoidal electromotive force.

The problem may be stated as follows: Given any network of circuits and an e.m.f. applied at any point in the system, what is the current at any time, *t*, after the electromotive force is applied?

CONSTANT E.M.F.

We may write

$$I = \frac{E}{Z(p)} \tag{1}$$

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* Communicated by General George O. Squier, Chief Signal Officer, U.S.A., and Associate Editor of this JOURNAL.

[1] " Oliver Heaviside Collected Papers," Vol. 2, p. 371, and " Electromagnetic Theory," Vol. 2, p. 127. See also J. R. Carson, *Physical Review,* 10, p. 217, and " The Theory of the Submarine Telegraph and Telephone Cable," Chap. 9, by H. W. Malcolm.

Where $Z\ (p)$ is the generalized impedance and $p = \frac{d}{dt}$ the time differential. $Z\ (p)$ may be an expression of any degree in p. We may put

$$Z(p) = (p-p_1)\,(p-p_2)\,(p-p_3)\ \ldots\ldots\ (p-p_m), \tag{2}$$

where $p_1, p_2\ \ldots\ldots\ p_m$ are the roots of the equation

$$Z(p) = 0. \tag{3}$$

By the use of partial fractions, we may put $\frac{1}{Z(p)}$ in the following form:

$$\begin{aligned} \frac{1}{Z\,(p)} &= \frac{1}{(p-p_1)\,(p-p_2)\,(p-p_3)\ \ldots\ (p-p_m)} \\ &= \frac{A}{p-p_1} + \frac{B}{p-p_2} + \frac{C}{p-p_3} + \ \ldots\ldots\ \frac{M}{p-p_m}. \end{aligned} \tag{4}$$

The constants $A, B, C, \ldots\ldots M$ are determined in the usual way

$$\left.\begin{aligned} A &= \frac{1}{(p_1-p_2)\,(p_1-p_3)\ \ldots\ldots\ (p_1-p_m)} \\ B &= \frac{1}{(p_2-p_1)\,(p_2-p_3)\ \ldots\ldots\ (p_2-p_m)} \\ &\ldots\ldots\ldots\ldots\ldots\ldots \\ &\ldots\ldots\ldots\ldots\ldots\ldots \\ M &= \frac{1}{(p_m-p_1)\,(p_m-p_2)\ \ldots\ldots\ p_m-p_{m-1}} \end{aligned}\right\} \tag{5}$$

The following notation is convenient:

$$\left.\begin{aligned} A &= \frac{1}{Z\,(p_1)} \\ B &= \frac{1}{Z\,(p_2)} \\ &\ldots\ldots \\ M &= \frac{1}{Z\,(p_m)} \end{aligned}\right\} \tag{6}$$

Substituting in (1), we get

$$I = E\left\{\frac{1}{(p-p_1)\,Z\,(p_1)} + \frac{1}{(p-p_2)\,Z\,(p_2)} + \ldots\ldots\ \frac{M}{(p-p_m)\,Z\,(p_m)}\right\} \tag{7}$$

Expanding the term $\frac{1}{p-p_1}$ we have

$$\frac{1}{p-p_1} = \frac{1}{p}\left\{1 - \frac{p_1}{p}\right\}^{-1} = \frac{1}{p}\left\{1 + \frac{p_1}{p} + \frac{p_1^2}{p^2} + \frac{p_1^3}{p^3} + \ldots\ldots\right\} \tag{8}$$

Operating on unity by $\frac{1}{p}$ which means integration with respect to t, we get

$$\frac{1}{p-p_1}=\frac{1}{p}\left\{1+p_1t+\frac{p_1{}^2t^2}{\underline{|2}}+\frac{p_1{}^3t^3}{\underline{|3}}+\cdots\cdots\right\} \qquad (9)$$

$$=\frac{1}{p}\,\varepsilon^{p_1t}$$

Operating on ε^{p_1t} by $\frac{1}{p}$ we obtain

$$\frac{1}{p-p_1}=\frac{1}{p}\,\varepsilon^{p_1t}=\int_0^t\varepsilon^{p_1t}dt=\frac{1}{p_1}\,\varepsilon^{p_1t}\Big]_0^t=\frac{1}{p_1}\left[\varepsilon^{p_1t}-1\right]. \qquad (10)$$

Applying the same process to each of the terms in equation (7), we finally get

$$1=E\left\{\frac{\varepsilon^{p_1t}}{p_1Z(p_1)}+\frac{\varepsilon^{p_2t}}{p_2Z(p_2)}+\cdots\cdots\frac{\varepsilon^{p_mt}}{p_mZ(p_m)}-\frac{1}{p_1Z(p_1)}-\frac{1}{p_2Z(p_2)}-\cdots\cdots\frac{1}{p_mZ(p_m)}\right\}. \qquad (11)$$

The above expression may be simplified in the following manner. Put

$$Z(p)=(p-p_1)\,F(p)$$

$$\frac{\partial Z(p)}{\partial p}=(p-p_1)\,\frac{\partial F(p)}{\partial p}+F(p)$$

$$F(p)=(p-p_2)\,(p-p_3)\,(p-p_4)\cdots\cdots\cdots(p-p_m)$$

For $p=p_1$ by (5)

$$\frac{\partial Z(p)}{\partial p}_{p=p_1}=F(p)_{\,p=p_1}=(p_1-p_2)\,(p_1-p_3)\cdots\cdots=Z(p_1) \qquad (12)$$

Similarly for the denominators in the other terms of (11),

$$\left.\begin{aligned}Z(p_2)&=\frac{\partial Z(p)}{\partial p}_{p=p_2}\\ Z(p_3)&=\frac{\partial Z(p)}{\partial p}_{p=p_3}\\ &\cdots\cdots\cdots\\ Z(p_m)&=\frac{\partial Z(p)}{\partial p}_{p=p_m}\end{aligned}\right\} \qquad (13)$$

Also if we put $p=0$ in (4) we get

$$\frac{1}{Z(p)_{p=0}}=-\left\{\frac{1}{p_1Z(p_1)}+\frac{1}{p_2Z(p_2)}+\cdots\cdots\frac{1}{p_mZ(p_m)}\cdot\right\} \qquad (14)$$

Substituting from (12), (13) and (14) in (11) we get the final formula

$$I=\frac{E}{Z(p)_{p=0}}+E\left\{\frac{\varepsilon^{p_1t}}{p_1\dfrac{\partial Z(p)}{\partial p}_{p=1}}+\frac{\varepsilon^{p_2t}}{p_2\dfrac{\partial Z(p)}{\partial p}_{p=2}}+\cdots\right\}$$

$$= \frac{E}{Z(p)_{p=0}} + \sum_{n=1}^{n=m} \frac{E\varepsilon^{p_n t}}{p_n \frac{\partial Z(p)}{\partial p}_{p=p_n}} \qquad (15)$$

Equation (15) is the form in which Heaviside gave the theorem in his "Electromagnetic Theory" (Vol. 2, page 127). $Z(p)_{p=0}$ is the algebraic function obtained by putting $p=0$ in $Z(p)$. It is the effective steady resistance to E. The term $\frac{\partial Z(p)}{\partial p}$ is the ordinary differential coefficient of Z with respect to p as a quantity and the summation to be extended to all the roots of the algebraic equation $Z(p)=0$. The summation term of equation (15) represents the transient current in system. Several illustrations of the application of this formula to the solution of electrical problems are given by Heaviside.

SINUSOIDAL E.M.F.

If the impressed e.m.f. is sinusoidal, of frequency $\frac{w}{2\pi}$, we can write

$$e = E\varepsilon^{jwt}$$

For brevity, put $jw=\lambda$, we have as in equation (1)

$$I = \frac{E\varepsilon^{\lambda t}}{Z(p)} \qquad (16)$$

$$I = E\left\{\frac{1}{(p-p_1)\,Z(p_1)} + \frac{1}{(p-p_2)\,Z(p_2)} + \cdots \frac{1}{(p-p_m)\,Z(p_m)}\right\}\varepsilon^{\lambda t} \qquad (17)$$

Operating by $\frac{1}{p}$ on the function $\varepsilon^{\lambda t}$, we have

$$\frac{1}{p}\varepsilon^{\lambda t} = \int_0^t \varepsilon^{\lambda t}\,dt = \frac{1}{\lambda}\varepsilon^{\lambda t} - \frac{1}{\lambda}$$

$$\frac{1}{p^2}\varepsilon^{\lambda t} = \int_0^t \left(\frac{1}{\lambda}\varepsilon^{\lambda t} - \frac{1}{\lambda}\right)dt = \frac{1}{\lambda^2}\varepsilon^{\lambda t} - \frac{1}{\lambda^2} - \frac{1}{\lambda}t$$

$$\frac{1}{p^3}\varepsilon^{\lambda t} = \int_0^t \left(\frac{1}{\lambda^2}\varepsilon^{\lambda t} - \frac{1}{\lambda^2} - \frac{1}{\lambda}t\right)dt = \frac{1}{\lambda^3}\varepsilon^{\lambda t} - \frac{1}{\lambda^3} - \frac{1}{\lambda^2}t - \frac{1}{\lambda}\frac{t^2}{\underline{|2}}. \qquad (18)$$

Repeating the process over and over, we get

$$\frac{1}{p^m}\varepsilon^{\lambda t} = \frac{1}{\lambda^m}\varepsilon^{\lambda t} - \frac{1}{\lambda^m} - \frac{1}{\lambda^{m-1}}t - \frac{1}{\lambda^{m-2}}\frac{t^2}{\underline{|2}} - \frac{1}{\lambda^{m-3}}\frac{t^3}{\underline{|3}} - \cdots$$

Expanding the term $\frac{1}{p - p_1}$, the denominator of the first term in (17), as in (8)

$$\frac{1}{p-p_1} = \frac{1}{p}\left(1 + \frac{p_1}{p} + \frac{p_1^2}{p^2} + \frac{p_1^3}{p^3} + \cdots \right\}$$

Operating on $\varepsilon^{\lambda t}$ and using the values given in (18) we get

$$\begin{aligned}\frac{1}{p-p_1}\varepsilon^{\lambda t} = \frac{1}{p}\Big\{ & \varepsilon^{\lambda_1 t} + \frac{p_1}{\lambda}\varepsilon^{\lambda t} - \frac{p_1}{\lambda} + \frac{p_1^2}{\lambda^2}\varepsilon^{\lambda t} - \frac{p_1^2}{\lambda^2} - \frac{p_1^2}{\lambda}t \\ & + \frac{p_1^3}{\lambda^3}\varepsilon^{\lambda t} - \frac{p_1^3}{\lambda^3} - \frac{p_1^3}{\lambda^2}t - \frac{p_1^3}{\lambda}\frac{t^2}{\underline{|2}} \\ & + \frac{p_1^4}{\lambda^4}\varepsilon^{\lambda t} - \frac{p_1^4}{\lambda^4} - \frac{p_1^4}{\lambda^3}t - \frac{p_1^4}{\lambda^2}\frac{t^2}{\underline{|2}} - \frac{p_1^4}{\lambda}\frac{t^3}{\underline{|3}} \\ & + \cdots\cdots\cdots\cdots\end{aligned} \tag{19}$$

Rearranging we get

$$\begin{aligned}\frac{1}{p-p_1}\varepsilon^{\lambda t} = \frac{1}{p}\Big\{ & \varepsilon^{\lambda t}\left(1 + \frac{p_1}{\lambda} + \frac{p_1^2}{\lambda^2} + \cdots\right) - \frac{p_1}{\lambda}\left(1 + \frac{p_1}{\lambda} + \frac{p_1^2}{\lambda^2} + \cdots\right) \\ & - \frac{p_1^2}{\lambda}t\left(1 + \frac{p_1}{\lambda} + \frac{p_1^2}{\lambda^2} + \cdots\cdots\right) \\ & - \frac{p_1^3}{\lambda}\frac{t^2}{\underline{|2}}\left(1 + \frac{p_1}{\lambda} + \frac{p_1^2}{\lambda^3} + \cdots\cdots\right) \\ & - \cdots\cdots\cdots\cdots\end{aligned}$$

The above is equal to

$$\frac{1}{1-\frac{p_1}{\lambda}}\,\frac{1}{p}\left\{\varepsilon^{\lambda t} - \frac{p_1}{\lambda}\left(1 + p_1 t + \frac{p_1^2 t^2}{\underline{|2}} + \frac{p_1^3 t^3}{\underline{|3}} + \cdots\right)\right\}$$

$$= \frac{1}{1-\frac{p_1}{\lambda}}\,\frac{1}{p}\left(\varepsilon^{\lambda t} - \frac{p_1}{\lambda}\varepsilon^{p_1 t}\right)$$

Operating again by $\frac{1}{p}$, we have finally

$$\frac{1}{p-p_1}\varepsilon^{\lambda t} = \frac{1}{\lambda - p_1}\left\{\varepsilon^{\lambda t} - \varepsilon^{p_1 t}\right\} \tag{20}$$

Extending the same operation to the other terms of (17), we get

$$\begin{aligned} I = E\varepsilon^{\lambda t} & \left\{\frac{1}{(\lambda-p_1)\,Z\,(p_1)} + \frac{1}{(\lambda-p_2)\,Z\,(p_2)} + \cdots\cdots\right\} \\ - E & \left\{\frac{\varepsilon^{p_1 t}}{(\lambda-p_1)\,Z\,(p_1)} + \frac{\varepsilon^{p_2 t}}{(\lambda-p_2)\,Z\,(p_2)} + \cdots\cdots\right\}\end{aligned} \tag{21}$$

By putting in equation (4) $p = \lambda$, we have

$$Z(p)_{p=\lambda} = \frac{1}{(\lambda - p_1)\, Z'(p_1)} + \frac{1}{(\lambda - p_2)\, Z'(p_2)} + \cdots\cdots$$

Substituting this value in (27), we get

$$I = \frac{E\varepsilon^{\lambda t}}{Z(p)_{p=\lambda}} - \sum_{n=1}^{n=m} \frac{\varepsilon^{p_n t}}{(\lambda - p_n)\, Z'(p_n)} \tag{22}$$

By (13) we have $Z'(p_n) = \frac{\partial Z(p)}{\partial p} p = p_n$, substituting this in (22), we get for the final expression

$$I = \frac{E\varepsilon^{\lambda t}}{Z(p)_{p=\lambda}} - \sum_{n=1}^{n=m} \frac{\varepsilon^{p_n t}}{(\lambda - p_n)\, \frac{\partial Z(p)}{\partial p}\, p = p_n} \tag{23}$$

Here again the first term, replacing λ by jw, represents the permanent state, the current in the system due to an impressed sinusoidal e.m.f. of frequency $\frac{w}{2\pi}$, and the second summation term the transient current before the permanent state is reached.

Determination of the Velocity of Alpha Rays from Polonium. Miss Irene Curie. (*Comptes Rendus*, July 24, 1922.)—The polonium employed had been separated from RaD by electrolysis and afterwards deposited on silver foil. The alpha rays emitted by the deposit passed in turn through two narrow slits so that only a sharply defined ray came through the second aperture. Upon the particles forming this ray acted a uniform magnetic field of about 10,000 gausses. Its direction was at right angles to the velocity of the particles. By it the paths of the particles were bent into circles whose radii were got from images recorded on a photographic plate in the presence and again in the absence of the field.

Two series of observations lead to the same value for the velocity of the alpha particles of polonium, 1.593×10^9 cm. per sec., or about one-sixth of the velocity of light. Alpha rays from polonium, according to Miss Curie's results, have .829 of the velocity of similar particles originating from RaC. The ranges of the two kinds of particles are from other experiments known to be, respectively, 3.925 and 6.971 cm. When Geiger's law that the ranges are in proportion to the cubes of the velocities is applied, the corresponding ratio of the velocities comes out equal to .826.

The frequent contributions of the present Lord Rayleigh to the literature of physics, the recent election of Captain Thomson, the son of Sir J. J. Thomson, to the chair of Natural Philosophy at Aberdeen and the work of Miss Curie in the field of radioactivity will furnish data for a study of the transmissibility of the acquired characteristic of ability in investigation. G. F. S.

BIOCHEMICAL OBSERVATIONS ON CERTAIN INSECTIVOROUS PLANTS.*

BY

JOSEPH SAMUEL HEPBURN, A.M., B.S. in Chem., M.S., Ph.D.

Secretary of the Section of Physics and Chemistry, Lecturer on Chemistry in the Hahnemann Medical College of Philadelphia.

NEPENTHES AND ITS PITCHER LIQUOR.

The *Nepenthaceæ,* or East Indian family of pitcher plants, consists of a single genus *Nepenthes* which includes a number of species. In the *Nepenthes,* the midrib is prolonged beyond the blade of the leaf as a tendril. The end of this tendril becomes evaginated or bulged to form a pitcher and its operculum or lid. As the pitcher and lid develop, they enclose a hermetically sealed space, the pitcher cavity, into which a liquor is secreted. Finally, when the pitcher has attained the proper stage of development, the lid opens and remains permanently in the open position.

After the lid has opened, insects are attracted by the nectar which is secreted by glands. These nectar glands occur on the outer surface of the pitcher, but are more abundant on the inner surface of the lid and on the inner edge of the corrugated rim that surrounds the top of the pitcher. The insects, which are attracted, are thus tempted downward into the pitcher, and pass to a richly glandular zone with a smooth surface—the so-called detentive surface. Here they lose their footing and fall into the pitcher liquor. The insects are then digested by the liquor.

Experimental evidence of the secretion of a proteolytic enzyme by the pitchers has been presented by Hooker,[1, 2] Tait,[3] von Gorup and Will,[4, 5] Vines,[6, 7, 8, 9, 10] Goebel,[11] Clautriau,[12] Fenner,[13] and Abderhalden and Teruuchi.[14] Other investigators—Tischutkin,[15, 16] Dubois,[17, 18] Couvreur,[19, 20] and Clément [21]—have deduced from their researches that the pitcher liquor does not contain a protease secreted by the plant, and that the digestion is due to bacterial action. Tests for the presence of enzymes, other than protease, have been made by comparatively few investigators. Tests for diastase were made by von Gorup and Will,[4, 5] by Vines,[6] and by Robinson; [22] the results were entirely negative.

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* Communicated by the Author.

Robinson[22] also tested for the presence of invertase, lipase and esterase, likewise with negative results.

The action of rattlesnake venom upon *Nepenthes* has been studied by John Marshall of the Robert Hare Laboratory of Chemistry at the University of Pennsylvania. In a personal communication to the author, dated March 29, 1920, Doctor Marshall states: "About twelve years ago I placed some rattlesnake venom in the pitchers of some *Nepenthes* in our botanical garden and found that nothing harmful resulted to the plant. I also injected some fresh venom into the tissue of the stalk of *Nepenthes* with no observable harmful effects upon the plant."

In previous communications,[23, 24] the author has described an extensive series of experiments concerning the presence of a protease in the liquor obtained from pitchers entirely free from insect captures. The liquor digested various proteins (edestan, carmine fibrin, protean of castor bean globulin, Jacoby's ricin) in the presence of dilute acid and a bactericide. Hence a protease was present. St. John and the author[25] found that the liquor of closed pitchers is bacteriologically sterile, while that of open active pitchers contains proteolytic bacteria; however, the digestion of proteins by these bacteria was an exceedingly slow process. The conclusion was drawn that the leading rôle in the digestion of the prey is played by the protease of the pitcher liquor, and that bacteria play but a secondary part in the digestion. The tissue enzymes of the captured insects may produce autolysis of their tissues, and thereby assist in the digestion.

The study has been extended to include tests for the presence of the following enzymes in the pitcher liquor: Catalase, urease, esterase, diastase, and the inverting enzymes (invertase, maltase, lactase, and emulsin). The liquor was obtained by means of a hypodermic needle and syringe from closed pitchers of plants growing in the Nepenthes House of the University of Pennsylvania. The needle was passed through the wall of the pitcher above the level of the liquor, then was pushed into the liquor which was immediately drawn into the barrel of the syringe. The tests for the presence of enzymes were begun immediately after the collection of the pitcher liquor.

In each test a blank or control experiment was made, using pitcher liquor which had been boiled to inactivate enzymes, then cooled to the temperature of the laboratory. In all other respects, each control was a duplicate of its determination proper. Trikresol was used as a bactericide in all the tests except that for catalase. The concentration of the trikresol in each reaction mixture was 0.2 per cent. Unless otherwise stated, the temperature of incubation was 37.5° C., and the period of incubation eight days.

View in Nepenthes House, Kew Gardens, England.

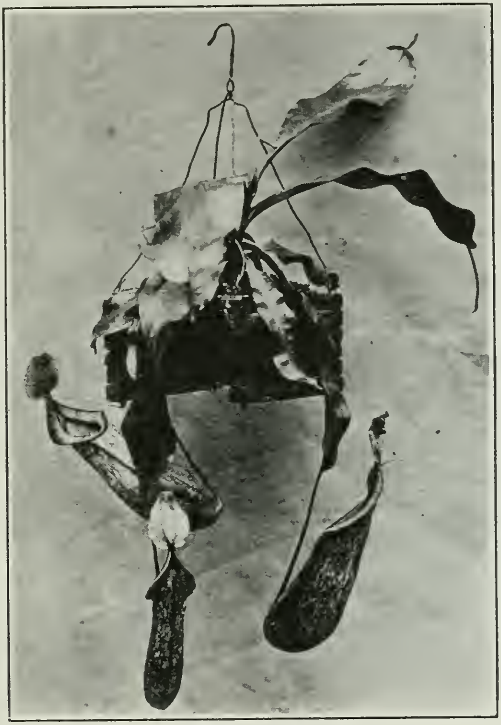
Catalase.—The pitcher liquor (2.5 c.c.) was placed in a test tube four inches in length, which was then filled with a 0.3 molar aqueous solution of hydrogen peroxide. The contents of the tube were well mixed; and the tube was then inverted over a pneumatic trough. At the end of one hour at room temperature, no oxygen gas had collected, hence catalase was absent.

Urease.—The pitcher liquor (5 c.c.) was mixed with an equal volume of a 1 per cent. aqueous solution of urea. After incubation, the determination proper and the control each required 0.20 c.c. of 0.1 normal sulphuric acid to render them neutral to methyl orange. Since the alkalinity of the determination proper did not exceed that of the control, the urea had not been cleaved by urease, and that enzyme was not present in the pitcher liquor.

Esterase.—The pitcher liquor (6.25 c.c.) was mixed with 4 c.c. of distilled water and 1 c.c. of ethyl butyrate. After the addition of the bactericide, both the determination proper and the control were rendered neutral to phenolphthalein by addition of 0.1 normal sodium hydroxide solution. After incubation, both the determination proper and the control required 0.05 c.c. of 0.1 normal sodium hydroxide solution to restore their reaction to the neutral point. Since the acidity of the determination proper did not exceed that of the control, enzymic cleavage of the ethyl butyrate had not occurred, and esterase was not present in the pitcher liquor. The absence of esterase would indicate the absence of lipase also, since these two enzymes are closely related, if not identical.

Diastase.—The pitcher liquor used in the test for this enzyme did not reduce Benedict qualitative alkaline copper solution; 4 c.c. of the liquor were mixed with an equal volume of a 1 per cent. aqueous solution of soluble starch. After incubation, both the determination proper and the control yielded the blue color of starch iodide with Lugol solution (iodine dissolved in an aqueous solution of potassium iodide), and both had absolutely no reducing action on the Benedict solution. Therefore, the starch had not been hydrolyzed, and diastase (amylase) was not present in the pitcher liquor.

Inverting Enzymes.—Preliminary tests showed that the pitcher liquor used in this series of experiments had no action on Benedict qualitative alkaline copper solution, and therefore did not contain reducing sugar. In each test for the presence of an inverting enzyme, 4 c.c. of the pitcher liquor were mixed with an equal volume of a 1 per cent. aqueous solution of the proper substrate, *i.e.,* sucrose for invertase, α-methyl *d*-glucoside for maltase, lactose for lactase, and amygdalin for emulsin. In the tests for invertase, maltase, and emulsin, after incubation, both the determination proper and its blank were permitted to act upon the Benedict solution. However, lactose reduces Benedict solution; therefore, in the test for lactase after incubation, both the determination proper and its blank were permitted to react with Barfoed solution at the temperature of boiling water for a period of twenty-five minutes. Barfoed solution (an aqueous solution of cupric acetate rendered acid with acetic acid) is not reduced under these conditions by the disaccharides including lactose, but is reduced by their cleavage products, the monosaccharides.

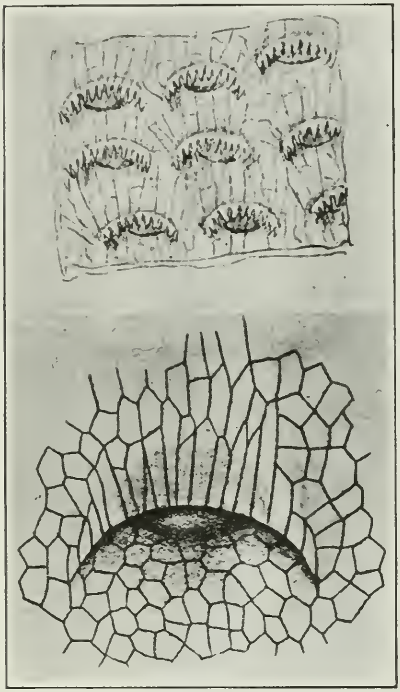


Nepenthes Dyeriana, showing the blade, the tendril, and the open pitcher of each leaf.

In the test for each of the four enzymes, neither the determination proper nor its blank reduced the copper solution; therefore, the inverting enzymes were not present in the pitcher liquor.

The presence of a protease in the pitcher liquor, and the absence of enzymes acting upon carbohydrates and fats, are evidence that the liquor is secreted in order to digest the proteins in the bodies of the captured insects, and thereby to supply the plant with nitrogenous food.

The pitcher plants include three families, subdivided into five genera. The family *Nepenthaceæ* contains one genus *Nepenthes;* the family *Cephalotaceæ*, one genus *Cephalotus;* and the family *Sarraceniaceæ,* three genera, *Heliamphora, Darlingtonia,* and *Sarracenia.* In another communication,[26] we have reviewed the work of previous investigators, and have described our own experiments which showed the presence of a protease in the pitcher liquor of six species of the genus *Sarracenia* and its absence from that of *Darlingtonia californica,* the only species of that genus. The most recent work of this nature on the genus *Cephalotus* is that of Dakin; [27] he has found a protease in the pitcher liquor of *Cephalotus follicularis*, the only species of that genus. Therefore, it may be concluded on both morphological and biochemical grounds that the pitchers of most, if not all, species of pitcher plants are designed for the capture and digestion of prey as a means of nutrition for the plant.



Digestive glands of *Nepenthes*, each inbedded underneath a projecting pocket-like flap. A group of the glands is shown in the upper section, a single gland at a higher magnification in the lower section.

Presence of Reducing Sugar.—The samples of pitcher liquor used in the tests for diastase and the inverting enzymes did not reduce Benedict qualitative alkaline copper solution. However, the liquor may at times reduce that solution. Twelve composite samples of liquor were collected from closed pitchers or from pitchers which had recently opened and were free from insects; nine of these samples reduced the Benedict solution, the other three samples had no action on that reagent. The type of pitcher, closed or open, had no influence on the response to this test. When reduction occurred, it was probably due to the presence of sugar derived from the nectar.

Tests for Anions.—A composite sample of liquor from closed pitchers was tested for the presence of chlorides and phosphates. It yielded a white curdy precipitate with silver nitrate solution. This precipitate was soluble in ammonia water, and was reprecipitated from the resulting solution on addition of nitric acid. Therefore chlorides were present. The liquor was digested with ammonium molybdate in the presence of nitric acid; a precipitate was not formed; therefore phosphates were absent. These results are in harmony with those obtained by Voelcker[28] in testing for these two acid radicals.

Test for Saponins.—According to Clautriau,[12] the pitcher liquor contains in solution a substance which causes insects to become wet and to sink. Saponins would confer this property upon the pitcher liquor if present in it, since they lower the surface tension. The hæmolysis test for saponins was therefore applied to liquor freshly collected from closed pitchers. The finger was pricked and blood was permitted to fall into 0.5 c.c. of a 0.1 per cent. solution of sodium citrate in a physiological (0.85 per cent.) solution of sodium chloride, until the volume of the latter had doubled. Equal volumes of the resulting suspension of human erythrocytes and the pitcher liquor were mixed on a glass slide, covered with a glass slip, and then examined through a microscope. The erythrocytes, or red corpuscles, remained intact at the end of thirty minutes; therefore hæmolysis did not occur, and saponins were absent from the pitcher liquor. In a control experiment, a dilute aqueous solution of digitonin, a saponin, was substituted for the pitcher liquor; complete hæmolysis occurred immediately.

DIONÆA MUSCIPULA.

The Venus fly trap, *Dionæa muscipula*, is an insectivorous plant, whose native habitat is in eastern North Carolina. It is the only species of the genus *Dionæa* which belongs to the family *Droseraceæ*. Therefore the Venus fly trap is closely related to the sun dews. In this plant, a foliaceous footstalk supports a bilobed leaf which is provided with a margin of spikes. Several trigger hairs, usually three, are present on the upper surface of each lobe. In the open leaf, the two lobes are at slightly less than a right angle to each other. When an insect comes upon the leaf, it may touch one of the trigger hairs, but nothing happens. As the insect moves about the leaf, it may touch the same trigger hair a second time, or it may touch another trigger hair. In either case, upon the second contact, the leaf snaps shut upon the insect.[31] The two lobes close, the midrib serving as a fulcrum; and the spikes interlock. A fluid is secreted; and the insect undergoes digestion. When digestion and absorption of its products are complete, the leaf again opens. Darwin[29] describes his own experiments on this plant, and also cites the work of others in his treatise on Insectivorous Plants.

Frank Morton Jones, of Wilmington, Delaware, collected both the secretion and the leaves from plants of *Dionæa muscipula* growing in their native habitat near Wilmington, North Carolina, at the end of the month of May, and presented them to the author for biochemical study.

Dionæa muscipula in its native habitat near Wilmington, North Carolina, showing both open and closed leaves. A leaf in the foreground has opened, but still contains the indigestible residue of its prey. Photograph taken by Charles W. Palmer and Walter Steckbeck, July 1, 1917.

The *secretion* was a composite sample gathered by means of a small pipette from fifty closed leaves containing captured insects. It was a glairy liquid, and was tested for the presence of a proteolytic enzyme. In one experiment, 0.3 c.c. of the secretion and 0.2 gram of carmine fibrin were added to 20 c.c. of an aqueous solution containing 0.2 per cent. hydrochloric acid and 0.2 per cent. trikresol; the carmine fibrin was completely dissolved on digestion for six days at the temperature of the laboratory. In another experiment, 0.3 c.c. of the secretion and 0.2 gram of carmine fibrin were added to 20 c.c. of an aqueous solution containing 0.5 per cent. sodium carbonate and 0.2 per cent. trikresol. The carmine fibrin was not even attacked during digestion for six days at the temperature of the laboratory. The proper control or blank experiments were also made, and showed no digestion of the substrate. These results indicate the secretion by the leaves of a protease which is active in the presence of a dilute acid. This protease doubtless digests proteins in the bodies of the captured insects, and thereby makes them available for absorption and the nutrition of the plant.

The entire *leaves* had been thoroughly washed in running cold water to remove the secretion, prey, and any foreign matter, and had been permitted to become air-dried. They were ground until the entire mass passed through a sieve with twenty meshes to the linear inch. This mass, which represented a composite sample of fifty or more leaves, was used for chemical analysis according to the methods of the Association of Official Agricultural Chemists.[30] The results are recorded in Table I. Crude fat is a synonym for ether extract. The soluble ash is that portion of the total ash which dissolved in boiling water, while the insoluble ash is the portion which was insoluble in that solvent; approximately one-third of the total ash was soluble. The alkalinity of the ash was also determined. The soluble ash present in 1 gram of the air-dried sample required 1.45 c.c. of 0.1 normal hydrochloric acid for its neutralization, while the insoluble ash required 6.14 c.c. These results were recalculated for the total solids; the solu-

TABLE I.

Percentage Composition of the Leaves of Dionœa Muscipula.

Constituent.	Air-dried Leaves.	Calculated on Water-free Basis.
Moisture	8.38	....
Total solids	91.62	100.00
Crude protein	8.31	9.07
Crude fat	11.18	12.20
Crude fibre	11.58	12.64
Nitrogen-free extractives	55.53	60.61
Total ash	5.02	5.48
Insoluble ash	3.32	3.62
Soluble ash	1.70	1.86

ble ash present in 1 gram of total solids required 1.58 c.c. of 0.1 normal hydrochloric acid for its neutralization, while the insoluble ash required 6.70 c.c. Methyl orange was used as an indicator in these titrations.

SUMMARY.

The liquor from pitchers of *Nepenthes,* which were entirely free from insect captures, contained a protease which exerted its activity in a slightly acid medium. Catalase, urease, esterase, diastase, invertase, maltase, lactase, and emulsin were not present in the pitcher liquor.

A substance, which reduced Benedict alkaline copper solution, was frequently, but not invariably, present in the pitcher liquor; it was probably sugar derived from the nectar.

The pitcher liquor contained chlorides, and did not contain phosphates and saponins.

A composite sample of the secretion of the leaves of *Dionæa muscipula* was examined, and was found to contain a protease which was active in the presence of 0.2 per cent. hydrochloric acid.

The leaves of *Dionæa muscipula* have been analyzed; and their composition is reported.

The author is indebted to Dr. Walter Steckbeck for the photograph of *Dionæa muscipula* and to Dr. John M. Macfarlane for those of *Nepenthes.*

BIBLIOGRAPHY.

[1] HOOKER: *Nature,* 1874, x, 366–372.

[2] HOOKER: Report of the Forty-fourth Meeting of the British Association for the Advancement of Science, 1874; Notes and Abstracts of Miscellaneous Communications to the Sections, 1875, 102–116.

[3] TAIT: *Nature,* 1875, xii, 251–252.

[4] VON GORUP and WILL: *Sitzungsberichte der physikalisch-medicinischen Societät zu Erlangen,* 1875–6, viii, 152–158.

[5] VON GORUP and WILL: *Berichte der deutschen chemischen Gesellschaft,* 1876, ix, 673–678.

[6] VINES: *Journal of Anatomy and Physiology,* 1876–7, xi, 124–127.

[7] VINES: *Journal of the Linnean Society, Botany,* 1877, xv, 427–431.

[8] VINES: *Annals of Botany,* 1897, xi, 563–584.

[9] VINES: *Annals of Botany,* 1898, xii, 545–555.

[10] VINES: *Annals of Botany,* 1901, xv, 563–573.

[11] GOEBEL: Pflanzenbiologische Schilderungen, Marburg, Elwert, 1893, ii, 186–193.

[12] CLAUTRIAU: Mémoirs couronnés et autres mémoires, publiés par l'Académie

Royale des Sciences, des Lettres et des Beaux Arts de Belgique, Collection in 8°, 1899–1900, lix, third memoir, 56 pages.

[13] Fenner: *Flora oder allgemeine botanische Zeitung*, 1904, xciii, 335–434 (especially pages 358–363).

[14] Abderhalden and Teruuchi: *Zeitschrift für physiologische Chemie*, 1906, xlix, 21–25.

[15] Tischutkin: *Berichte der deutschen botanischen Gesellschaft*, 1889, vii, 346–355.

[16] Tischutkin: *Botanisches Centralblatt*, 1892, l, 304–305.

[17] Dubois: *Comptes rendus des séances de l'Académie des Sciences*, 1890, cxi, 315–317.

[18] Dubois: *Comptes rendus des séances et mémoirs de la Société de Biologie*, 1903, lv, 232–233.

[19] Couvreur: *Comptes rendus des séances de l'Académie des Sciences*, 1900, cxxx, 848–849.

[20] Couvreur: *Annales de la Société linnéenne de Lyon*, 1900, Nouvelle série, xlvii, 81–83, published 1901.

[21] Clément: *Annales de la Société linnéenne de Lyon*, 1915, Nouvelle série, lxii, 11-14, published 1916.

[22] Robinson: *Torreya*, 1908, viii, 181–194.

[23] Hepburn: *Proceedings of the American Philosophical Society*, 1918, lvii, 112–129.

[24] Hepburn: *Contributions from the Botanical Laboratory of the University of Pennsylvania*, 1919, iv, 442–451.

[25] Hepburn and St. John: *Contributions from the Botanical Laboratory of the University of Pennsylvania*, 1919, iv, 451–457.

[26] Hepburn, St. John and Jones: JOURNAL OF THE FRANKLIN INSTITUTE, 1920, clxxxix, 147–184.

[27] Dakin: *Journal and Proceedings of the Royal Society of Western Australia*, 1917–1918, iv, 37–53, published 1919.

[28] Voelcker: *Annals and Magazine of Natural History*, 1849, Series 2, iv, 128–136.

[29] Darwin: Insectivorous Plants, 2nd Edition, New York and London, Appleton, 1915, Chapter xiii, pp. 232–260.

[30] Official and Tentative Methods of Analysis of the Association of Official Agricultural Chemists, Revised to November 1, 1919. Washington, 1920.

[31] Macfarlane: *Contributions from the Botanical Laboratory of the University of Pennsylvania*, 1892, i, 7–44.

CONSTANTINE HERING LABORATORY,
HAHNEMANN MEDICAL COLLEGE,
PHILADELPHIA, PA.

The Production of Nitric Oxides and Ozone by High Voltage Electric Discharges.—In Bulletin 9 recently issued by Purdue University, KARL B. MCEACHRON and R. H. GEORGE give in much detail the results of experiments made at the University during the war and somewhat later, to determine conditions which promote the fixation of nitrogen with oxygen, a problem of great importance in industrial chemistry. It was found that methods for absorption of the gas could be devised which are much simpler than those heretofore in use, and that the amount of equipment was much less. Ozone was produced in almost all the experiments and the data in regard to it have been included. The pamphlet covers 190 pages, including a good index and many diagrams and illustrations.

Some of the conclusions are as follows: Using fresh dry air on Siemens type of tubes, the application of a sufficiently high potential from either an induction coil or a high voltage transformer, will cause a decrease in pressure (the experiment being made with a closed volume of air) which shows a contraction of volume. After reaching a certain point, however, the action reverses, a result that had already been noted by Spiel.

1. Holding conditions as constant as possible the reversal points on check runs do not agree closely with respect to either time or reversal or the amount of pressure decrease. The yield of nitric acid is always much greater near the reversal point than after the pressure has increased up to the initial.

2. In case the air in the tube has been in contact for a considerable time with other air, even in minute quantities, which has been previously subjected to electrical discharge, the pressure decrease is modified or may be eliminated altogether, the pressure rising instead of falling. Such contamination decreases the yield and may under certain conditions prevent the formation of any absorbable products. The appearance of the discharge is greatly modified by such contamination.

3. It was found that the pressure decrease is not proportional to the nitric oxides absorbed. It has not been possible in most cases to account for more than a fractional part of the pressure decrease on the basis of the amount of ozone and nitric acid found. This seems to indicate the presence of some heavy molecule, which is not being absorbed.

4. As a rule the pressure did not decrease more than 60 mm. below the initial pressure, but in one case the decrease was 114 mm., the pressure characteristic being almost a straight line. It has not been possible to duplicate this run. The yield at a point near reversal was much less than that obtained from other runs with a decrease of pressure of not over 30 mm. When taking the probable temperature of the gas into account, the contraction in this run amounts to nearly one-fifth by volume.

5. Alternating current seems in most cases to cause a more rapid pressure decrease than does current from an induction coil having approximately the same effective value. This condition is most pronounced when the time of exposure is relatively short.

H. L.

THE STABILITY OF ATOM NUCLEI, THE SEPARATION OF ISOTOPES, AND THE WHOLE NUMBER RULE.*

BY

WILLIAM D. HARKINS, Ph.D.

Department of Chemistry, University of Chicago.

54. THE DISCOVERY OF THE ISOTOPES OF NEON.

In 1906 Boltwood of Yale discovered a new radioactive element which he called ionium.[70] This exhibited chemical properties similar to thorium, and is so much like the later that Marckwald and Keetman of Berlin were unable to obtain the slightest detectable separation of the two elements in experiments which involved years of labor.[71] A number of other "isotopic radioactive elements" were discovered in the years which followed, but the first experimental indication of the possible existence of isotopes, among the non-radioactive elements, was obtained by Sir J. J. Thomson, of Cambridge, as described in his address to the Royal Institution on Friday, January 17, 1913, in which he says:

"I now turn to the photograph of the lighter constituents; here we find the lines of helium, of neon (very strong), of argon, and in addition there is a line corresponding to an atomic weight 22, which cannot be identified with the line due to any known gas. I thought at first that this line, since its atomic weight is one-half that of CO_2, must be due to a carbonic acid molecule with a double charge of electricity, and on some of the plates a faint line at 44 could be detected. On passing the gas slowly through tubes immersed in liquid air the line at 44 completely disappeared, while the brightness of the one at 22 was not affected.

"The origin of this line presents many points of interest: There are no known gaseous compounds of any of the recognized elements which have this molecular weight. Again, if we accept Mendeleef's Periodic Law, there is no room for a new element with this atomic weight. The fact that this line is bright in the sample when the neon line is extraordinarily bright, and invisible in the other when the neon is comparatively feeble, suggests that it may possibly be a compound of neon and hydrogen, NeH_2, although no direct evidence of the combination of these inert gases has hitherto been found. I have two photographs of the discharge through helium in which there is a strong line, 6, which could be explained by the compound HeH_2, but as I have never again been able to get these lines, I do not wish to lay much stress on this point. There is, however, the possibility that we may be interpreting Mendeleef's law too rigidly, and that in the neighborhood of the atomic weight of neon there may be a group of two or more elements with similar properties, just as in another part of the table we have the group iron, nickel, and cobalt. From the relative intensities of the 22 line and the neon line, we may conclude that the quantity of the gas giving the 22 line is only a small fraction of the quantity of neon."

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* Continued from page 681, vol. 194, November, 1922.

[70] Boltwood: *Am. J. Sci.*, **22**, 537 (1906), **24**, 370 (1907).

[71] Keetman: *Jahr. Radioactivität*, **6**, 269 (1909).

While the evidence obtained for the existence of two isotopes of neon seems now to have been very good, it is said that for many years Thomson himself remained doubtful of their existence. A letter written on May 5, 1919, by Dr. F. W. Aston, Thomson's former assistant, states: "For my own part, I am fairly confident of the existence of neon and meta-neon, but I do not consider that the results so far warrant a definite statement to the public. It is a pity that several authors of text-books seem to have jumped to the conclusion that such has been made."

Thomson's results suggested to Aston that it might be possible to separate neon by distillation from charcoal, or by diffusion. The former method gave no separation, but the latter gave light and heavy fractions of different densities. However, the volume of the extreme fractions was so small, only 2 and 3 c.c., that Aston himself was very doubtful of the result,[72] and did not publish the details of his work until many years later. While Aston undoubtedly secured a slight separation of the isotopes, it is possible that a part of the density change was due to impurities, which are very difficult to exclude from such small fractions, particularly in the case of a gas such as neon.

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[72] Aston: *Report British Assoc. Adv. Science*, 1913, p. 403.

55. DISCOVERY OF THE ISOTOPES OF CHLORINE BY HARKINS AND BROEKER (ACTUAL SEPARATION BY THE DIFFUSION METHOD), AND BY ASTON (POSITIVE RAY METHOD).

In 1916 Harkins and Turner began experimental work upon the separation of chlorine into isotopes by the diffusion of gaseous chlorine, in order to demonstrate the correctness of the idea of Harkins and Wilson,[73] that the atomic weights of the chemical elements are good evidence of the existence of isotopes in *chlorine, magnesium,* and *neon,* and in most elements of atomic numbers 28 to 82, particularly in those of even atomic number in this range. The beginning of the experimental work on the separation was announced in the *Journal of the American Chemical Society* in 1916. Since there are two atoms of chlorine in Cl_2, the separation of isotopes should be only one-half as fast with this gas as when hydrogen chloride gas is used. Notwithstanding this fact, it was at first thought that the ease of condensation of the chlorine would compensate for the difference. Though slight density changes were obtained by the first set of repeated diffusions, it was difficult to prove that these were not due to impurities. In order to hasten the separation, which had been stopped by the war, Doctor Turner, in the summers of the years 1917 and 1918, and Mr. Liggett, in the year 1917–18, changed to the diffusion of hydrogen chloride gas. While some separation of the isotopes of chlorine was undoubtedly secured, as was proved by later work on the changes of density, no atomic weight determinations were made at this time. In October, 1919, Harkins and Broeker began the diffusion of HCl gas in the apparatus made by Doctor Turner, and, *in January, 1920, 10 grams of hydrogen chloride, the chlorine of which showed an atomic weight of 35.515, had been obtained,* together with a considerable quantity of the gas containing chlorine of a lower atomic weight than that of the ordinary element. Five atomic weight determinations indicated increases of atomic weight over that of normal chlorine, of 0.052, 0.059, 0.057, 0.055, and 0.053 units. A notice of this separation was published in the February number of the *Physical Review,* and in *Science* and *Nature.*[74] While a preliminary notice of Aston's results on the positive ray analysis of chlorine was published about six weeks[75] before the publication of our separation, it should be recognized that the chemical methods are much slower than the determinations by the positive ray apparatus, so without doubt the writer and his collaborators had separated chlorine into isotopes *before* Aston had obtained their positive ray analysis. In this connection it should be remembered that the idea that chlorine consists of isotopes, and a notice of the beginning of the separation, had both been published by the writer four and one-half years before Aston made any statement in regard to isotopes in chlorine.

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[73] *J. Am. Chem. Soc.,* 37, 1371, 1390 (1915).

[74] *Physical Review,* 15, 74 (Feb., 1920); *Science,* N. S., 51, 289–91 (1920); *Nature,* 105, 230–1 (1920).

The apparatus used in the separation of the heavy chlorine consisted of 12.2 metres of churchwarden pipe stems, contained in glass tubes and boxes, in which the diffusion was carried out, while the three sets of apparatus for the light fraction were smaller. A somewhat similar apparatus will be described in section 58.

Three months after the publication of the notice of the separation of the isotopes of chlorine, the work, which was proceeding with great rapidity, was stopped by the death of Mr. Broeker. No increase in the atomic weight of the heavy fraction had been obtained since January, since the whole endeavor had been put upon enlarging the quantity of material, which, for the heaviest fraction, had risen to 20 grams. *The relative increase in density, 1 part in 645, is by far the largest yet attained for any element, and the quantity of the final fractions is much greater than that secured later in the case of mercury. This was the first investigation, also, in which appreciable amounts of isotopic material were obtained.*

The chlorine used in the atomic weight determinations was highly purified by methods which will be described in a later section. The efficiency of the process was about 60 per cent.; that is about 60 per cent. of the theoretical change of atomic weight was actually obtained. In calculating the separation to be expected, it was necessary to assume the atomic weights for the individual isotopes. In accordance with the assumption of Harkins and Wilson,[76A] the atomic weight of the lower isotope was taken as 35, and corresponding with their idea that the difference in the atomic weights of isotopes is most commonly

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[75] *Nature*, Dec. 18, 1919.

[76] *Loc. cit.*, (A) page 1391; (B) pages 1389–90 (1915).

2,[76B] it was supposed that the most probable weight for the heavier isotope would be 37, which agrees with the weight afterward found.

56. SEPARATION OF THE ISOTOPES OF CHLORINE BY HARKINS AND HAYES.

In order to confirm the separation of chlorine into isotopes as obtained by Harkins and Broeker, it seemed advisable to continue the work on the diffusion of hydrogen chloride gas. Due to the fact that Mr. Broeker had, just previous to his death, adopted an improved, but partly unknown, system of labelling the fractions from his diffusion, it was decided to begin with material of the ordinary atomic weight. This was diffused in an apparatus (see section 58), which has a capacity of 1000 litres of HCl gas, at ordinary pressures, per day. In this way 9 g. of atomic weight 35.498 and 90 g. of atomic weight 35.494 were obtained by the summer of 1921. In addition there was prepared 400 g. of atomic weight about 0.02 unit higher and about 4 kilos of about 0.01 unit higher than ordinary chlorine. The atomic weight determinations were made by the method of Harkins and Broeker, and will be described in sections 59 to 65.

57. SEPARATION OF THE ISOTOPES OF CHLORINE BY HARKINS AND LIGGETT.[77]

In 1917–18 T. H. Liggett and the writer diffused HCl gas in an apparatus similar to that used later by Harkins and Broeker. The separation was interrupted and the atomic weight determinations delayed by the illness of Mr. Liggett. Later work at Central College, in Pella, Iowa, gave chlorine of an atomic weight 35.505 with an increase of 0.045 in the atomic weight over that of ordinary chloride.

The atomic weight determinations were made by the standard method of determining the weight of silver chloride precipitated from a known weight of silver, dissolved as silver nitrate. In each case the determination with ordinary chlorine and the one with the isotopic chlorine were made side by side by the same methods. The chlorine was added in the form of extremely pure potassium chloride, and after long standing the silver chloride was filtered off on a Monroe crucible (a platinum crucible in which the filtering medium is a thick platinum sponge). The silver chloride was washed while ice cold with ice cold water containing 5 c.c. of 6 *N* nitric acid per litre, and the very small (about 0.00008 g.) correction made for the silver chloride thus dissolved. A perforated platinum disc was kept over the platinum sponge. The crucible with the precipitate was heated at 250° in an electric oven for 10 hours, cooled three hours in a dessicator placed beside the balance, and then weighed. It was heated again, this time for two hours, and cooled and weighed as before. The major portion (90 to 98 per cent.) of the precipitate was then removed from the top of the platinum disc by means of a small metal spatula, and put in a quartz crucible. After weighing, the crucible with the precipitate was heated to 250°, cooled and weighed, and if the loss of weight was greater than 0.00002 gram, it was heated again until the weight became constant. The quartz crucible was then set inside a nickel crucible and heated until the silver chloride fused into one mass. The crucible was rotated to prevent the inclusion of gas bubbles, cooled in a dessicator and weighed. It was then fused again to make sure the weight had become constant. The fusion correction determined in this way was usually about 0.00006 g. per gram of silver chloride.

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[77] A more complete account of this work, and especially of the precautions used in the atomic weight determinations, will be published later in the *Journal of the American Chemical Society.*

Weighing.—The balance was a high sensitivity analytical balance made by Ainsworth, and it was found that by taking the null point both before and after the weighings, the samples of silver, for example, could be weighed with not more than 1/100 mg. difference between the weighings. The weights were constantly compared with Class M weights standardized by the U. S. Bureau of Standards.

Purification of the Chlorine.—The solution of hydrogen chloride in pure water, obtained from the diffusions, was distilled in an apparatus of hard glass, and the middle fraction used for further purification. No bromine or iodine could be detected by very careful tests. However, to insure their absence the hydrochloric acid was distilled after a few crystals of potassium permanganate had been added to it, and the middle fraction was used for further purification. The acid was converted to potassium chloride by adding potassium carbonate which had been prepared from quite pure material by several careful recrystallizations in which the amount of the carbonate was reduced to 1/50 its original weight. The potassium chloride thus formed was recrystallized a number of times from very pure water. Both the isotopic and the ordinary chlorine were purified in this way.

Tests for Iodine and Bromine.—Numerous tests were made upon both the fractions and the mother liquors in the several stages of the purification process, but at no time could either iodine or bromine be detected in the isotopic material. For iodine both the nitrous acid and the nitrosyl sulfuric acid test were used. The former would easily detect 1/100 milligram of iodine in 0.8 g. of potassium chloride, while the later would detect 1/10 mg. in the same amount of potassium chloride. It was found that under the same conditions, that is, in the presence of potassium chloride, the chlorine water and carbon bisulphide test would detect 1/10 mg. of bromine when properly used. Since bromine was not found in the mother liquors nor in the purified material, its absence, except in entirely negligible amounts, is certain.

Atomic Weight of the Isotopic Chlorine.—The final heavy fraction from the diffusion gave 3.08 grams of potassium chloride, with a cut of 14,700. This cut should give, in a diffusion which is 100 per cent. efficient, a separation of 0.0912 unit of atomic weight. Actually the separation was 0.045 unit of atomic weight, or the efficiency of the process was 50 per cent., which is slightly lower than that attained by Harkins and Broeker and higher than that of Harkins and Hayes. It will be seen later that the lower efficiency in the last investigation mentioned was due to the fact that the pores in the porcelain tubes used were larger than in the two other sets of experiments. Table XXXVIII A gives the values obtained in atomic weight determinations on the different fractions.

TABLE XXXVIII A.

Atomic Weight Determinations on Isotopic Chlorine by the Standard Method of Precipitation of Pure Silver by Means of the Chloride.

Diffusion.	Approximate Cut.	Atomic Weight.	Mean Atomic Weight.	Over Ordinary Chlorine Increase in Atomic Weight Theory.	Expt.
1		35.466			
		35.473	35.470		0.010
2		35.483			
		35.491	35.487		0.027
3	14,700	35.502			
		35.508	35.505	0.0912	0.045

58. APPARATUS FOR THE SEPARATION OF CHLORINE INTO ISOTOPES BY DIFFUSION THROUGH A POROUS WALL AT ATMOSPHERIC PRESSURE, AS USED BY HARKINS AND HAYES.

Of the methods for the diffusion of a gas through a porous wall, there is little doubt that the most efficient is what is termed a vacuum diffusion, in which the gas diffuses through the wall into as high a vacuum as can be maintained. The pressure on the high pressure or " heavy fraction " side of the wall is kept at a magnitude which is dependent upon the diameter of the pores in the wall, and at such a value (for example, 10 mm. of mercury) that the mean free path of the gas is as great as the diameter of the pores, which should be of uniform diameter. The low pressure of the gas insures not only a molecular passage of the gas through the pores, but it also aids greatly in securing a good mixing of the gas.

There are, however, several objections to the diffusion at low pressures: (1) it is difficult to make the process automatic; (2) the volume of the gas per unit mass is greatly increased, and (3) it necessitates a more cumbersome method of collecting the heavy and light fractions. For these reasons it was decided, since a fair efficiency had been obtained in a separation of known gases, and particularly since a very good (about 60 per cent.) efficiency had been obtained in the separation of the isotopes of chlorine by Mr. Broeker by diffusing at atmospheric pressure, to delay the use of the vacuum method[78] until after the difference in atomic weight of the chlorine separated by this method had been definitely established by the use of this partly automatic apparatus.

The general procedure adopted is to generate hydrogen chloride at atmospheric pressure by dropping concentrated sulfuric acid into concentrated hydrochloric acid from a height of about 90 cm. in order to secure good mixing of the acids. For later diffusions the sulfuric acid is dropped upon sodium chloride. The dried gas is passed through porous porcelain tubes, and the lighter fraction which consists of the diffusate which passes through the walls is swept away by a rapid current of purified air. The heavy fraction is that which passes through the system of tubes and remains inside. Both fractions are absorbed by condensation in the *surface* of a considerable amount of water. The apparatus, though quite similar to that used in this laboratory by Doctor Turner and by Mr. Broeker, but not described by them, is greatly improved in many particulars. It was designed to care for 1000 litres of hydrogen chloride per day, at atmospheric pressure.

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[78] Two low pressure diffusion apparatuses, for the separation of HCl into isotopes, have been constructed in this laboratory, one by Mr. Mann, and the other by Mr. Harris. One of these is now in use.

Only acids of high purity were used in the work, and the hydrogen chloride produced came in contact only with pure sulfuric acid, glass, porous porcelain, and a very small area of paraffin, from the time it left the generators until it was absorbed in distilled water of " conductivity " grade.

Since according to the Rayleigh theory the enrichment of the heavy fraction with respect to the heavy constituent depends only upon the fraction of the original gas that remains inside the diffusion tubes, and since this fraction changes very rapidly with the rate at which the gas is fed into them from the generator, a flowmeter was placed in the line leading from the generator, and the evolution of gas was so regulated that the flowmeter gave a constant reading.

Flowmeters were also placed in all of the air sweep-out lines for each diffusion tube jacket, since it was necessary to reduce the partial pressure of the hydrogen chloride in the diffusate to a very low value as soon as it escaped from the walls of the diffusion tubes, and since otherwise a back diffusion would greatly lower the efficiency of the process.

A 20-litre bottle (1), with a tall dropping head, serves as a generator for the first diffusion. Six litres of C. P. hydrochloric acid is introduced into this bottle through the dropping funnel (2). For each 6 litres of this acid about 8 litres of concentrated C. P. sulfuric acid is dropped into it from a very wide 24-litre supply bottle (3). The flow of acid, after it is started, is controlled by the 3-way stopcock (4), the supply being sufficient to run for 23 hours. By refilling the generator at about 4.00 P.M. each day, a very steady flow of gas is secured through the night, the regulation requiring no attention between 10.00 P.M. and 7.30 A.M. When the speed of generation begins to fall in the morning, the generator is heated to 50° by means of an air-bath heated on an electric hot plate. By this means 75 per cent. of the hydrochloric acid in the original acid can be recovered. The generator is emptied by means of pressure through the siphon (4) directly into a carboy. For all succeeding diffusions the gas is generated in a 2-litre or a still smaller flask (5) into which sulfuric acid is dropped from a funnel (6). When the speed of evolution of gas from this generator falls, it is heated to 100°, thus giving nearly 100 per cent. recovery of the hydrogen chloride.

The trap (7) is to prevent an explosion of the generator, which otherwise is likely to occur if the generator happens to foam over, since the warm sulfuric acid solution of sodium hydrogen sulfate will solidify very quickly when it reaches the cold tubes. This usually clogs the tubes, and an explosion is apt to result, but has never occurred when the trap is in the system.

From the generators the hydrogen chloride passes into the trap (8) which collects moisture and sulfuric acid spray and through the flowmeter (9). Sulfuric acid is used as the manometer liquid in all of the flowmeters, and its injection into the apparatus is prevented by the traps (10). The bulb (11) is used to prevent sulfuric acid from being drawn back into the flowmeter (10) from the gas dryer (12). The thistle tube and its connections on (12) served to introduce fresh acid into the dryer, and also as a manometer to measure the pressure at the generator end of the diffusion train. The drying acid in (12) is renewed every second day. The bulb (13) is filled with glass wool, tightly packed, to filter out all sulfuric acid spray from the dried gas. After passing this the gas goes directly into the first diffusion tube (14). The first diffusion tubes are the stems of churchwarden pipes, while the succeeding ones were especially prepared for our use by the Ceramics Division of the Bureau of Standards. The latter are one metre long, 11 mm. outside diameter, with 2 mm. walls. They are sealed into glass tubes of almost the same diameter by the use of plaster-of-Paris. The diffusion tubes are then sealed into glass jackets 1.5 metres long, and 5 cm. in diameter. The air for sweeping out the diffusate enters the jackets through the two tubes (15) and passes out of it through the three tubes (16). These three exit tubes for each jacket are assembled into a single line leading to the absorbers for the light fraction. During the first diffusion the material from the first diffusion unit is absorbed in distilled water in absorber (17) and is designated as the light fraction from the first diffusion. During later diffusions of the heavy fraction this absorber is shunted out of the line, since its capacity is too great. The diffusate from the succeeding 4 jackets is absorbed in the large absorber (18) and when the concentration of the solution reaches 6 *N*, it is turned back into the stock of the laboratory (not, however, for any diffusion after the first) as diluted chemically pure hydrochloric acid. It is free from sulfites, sulfates, organic matter, and gives no test for iodine or bromine. The heavy fraction, or that which remains inside of the tubes at the end of the fifth or last unit, is absorbed in the absorber (19).

In the third and fourth diffusions only the first two units are used, and the small absorber (20) is used for the heavy fraction. Very large 3-way stopcocks (22) are between each two diffusion units, so that the apparatus may be used as two or more separate diffusion trains. The series of bulbs and the dropping funnel (21) constitute a sulfuric acid dryer for the heavy fraction passing from the fifth unit to the absorber (19), its purpose being to prevent any moisture from the absorber from reaching the porous tubes. The absorbers were all made on the same plan, and consist of two or more horizontal, and usually very large, glass tubes, arranged one above the other. Each of these tubes is provided with a gas inlet tube at one end, and an outlet tube at the other, and also with a tube and stopcock for allowing the acid to be dropped into the next unit below, or, on the bottom or first unit, for drawing it off from the apparatus.

The horizontal tubes are filled nearly full of pure distilled water, thus leaving a long narrow passage for the gas. Nearly all of the hydrogen chloride is absorbed in the first unit, and none of this gas can be detected by the odor at the exit from the last tube. When the solution in the first or bottom tube reaches 6 *N* in concentration, it is drawn off, the solution in each of the other tubes is dropped into the tube just below it, and distilled water is poured into the last or uppermost tube. This change can be made during the operation of the apparatus, while the method of surface absorption makes it possible to keep the pressure in the tubes very close to that of the external atmosphere, and to balance properly the pressures inside and outside the tubes, so that capillary transpiration may not occur.

The air supply for sweeping out the diffusate from the jackets comes from the compressed air supply of the laboratory, and is passed into an empty bottle (23) for settling out impurities, then through 30 per cent. caustic soda solution in the very large bottle (24), through the safety bottle (25), through concentrated sulfuric acid in a very large bottle (26), and is then blown on the surface of concentrated sulfuric acid in the bottle (27). It is then filtered through a foot of glass wool (28) and a foot of absorbent cotton (29), and passes into the distribution line (30). From this it flows through individual stopcocks (31), through flowmeters (32), past sulfuric acid manometers (33), through traps (34) into the jackets of each unit. The traps are used to prevent sulfuric acid from getting into the diffusion units from the manometers or flowmeters. The manometer (35) and that at (12) serve to give the gas pressure in the diffusion line, while those designated as (33) indicate that in the jackets.

Air is passed through each jacket at the rate of 3 litres per minute. During first diffusion hydrogen chloride passes flowmeter (9) at the rate of 600 c.c. per minute, and at this rate one-thirtieth of it arrives at the absorber for the heavy fraction (19) and is collected there. For the second diffusion, gas is generated at the same rate, but only four of the units are used. This gives a cut of 20. Third diffusions are run with only the first two units, gas being generated at the rate of 200 c.c. per minute, and again a cut of 20 results. The total cut 30 × 20 × 20, or 12,000, should, according to the Rayleigh theory, give an atomic weight for the chlorine in the heavy fraction of 35.54, but it is hardly to be expected that an efficiency of 100 per cent. in terms of this theory can be obtained, except possibly in a vacuum diffusion under ideal conditions.

The heavy fraction from each diffusion is neutralized with very pure sodium hydrogen carbonate, and is used in the generator which uses salt (5) for the regeneration of the hydrogen chloride. It is found that the generation from sodium chloride occurs at a more uniform rate if carried out at a temperature of 80° until the charge is nearly spent, when the temperature is rapidly raised to 100°. If the generator at the middle of the run is giving off gas at the rate of over 300 c.c. per minute, the salt cake will adhere to the bottom of the flask, until enough sulfuric acid has been run in to float it. Just as it comes loose from the bottom of the flask there is a violent evolution of gas.

At rates below 300 c.c. per minute the cake is gradually wetted throughout with sulfuric acid and the difficulty is avoided.

It is evident that the process of diffusion may be carried out fractionally and this was done. Thus the light fraction from the second diffusion has nearly as high a density as the heavy fraction from the first diffusion, so it is not rejected, but is rediffused, and the heavy fraction which results has nearly as high a density as that of the original second diffusion.

59. METHOD OF ANALYSIS AND CALCULATION OF RESULTS.

In order to be able to determine the effects of the successive diffusions it is important to develop a method of determining with considerable precision the change of atomic weight produced. It was found that such a method could be devised easily, provided a simple and seemingly accurate hypothesis is adopted as its basis. This is that isotopes have so nearly the same atomic volumes and the same chemical properties, that no error of sufficient magnitude to affect the analyses will be introduced if it is assumed that they are exactly alike in these respects. That the isotopes of lead have the same volume within the limits of the experimental error has been shown by Soddy[79] and by Richards[80] and that their identity in chemical properties is almost complete is demonstrated by the work on the spectra of the isotopes of lead described in section 53 of the present paper, which shows the identity in this respect to one part in a million.

However, even though this hypothesis is used as a basis for calculation, the proof that a *separation* of the two isotopes of chlorine has been made is *entirely independent* of the assumption, since no differences of atomic volume could be detected unless a separation had first been effected.

The simplest method for determining the increase of atomic weight was thought to be the determination of the densities of specimens of highly purified ordinary hydrochloric acid, and a comparison with these of the density of a specimen of acid produced by diffusion, which will be termed the isotopic acid. The plan adopted was to fix the molecular concentrations of these two acids as determined by titration, at the same value, and to compare the weights of hydrogen chloride which they contain. It is evident that the weight of the isotopic acid should be greater than that of the ordinary or "comparison" acid, since the present discussion refers to the heavy fraction. These weights are in the same ratio as the formula weights of hydrogen chloride in the two solutions, so

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[79] Soddy: *Nature*, **94**, 615 (1915).

[80] Richards: *J. Am. Chem. Soc.*, **38**, 221 (1916); and "Presidential Address to the American Association for the Advancement of Science," 1918.

$$M_i = 36.468 \;.\; W_i/W_c \qquad (1)$$

and

$$A_i = M_i - 1.008 \qquad (2)$$

or

$$\triangle A = 36.468 \triangle W/W_c. \qquad (3)$$

Here M_i and A_i are the molecular weight of hydrogen chloride and the atomic weight of chlorine, respectively; W_i and W_c are the weights in grams of the hydrogen chloride in the same volumes (*e.g.*, pycnometer full) of the comparison and the isotopic acids, and ΔW is the increase in weight which occurs when the isotopic acid is substituted for the comparison acid. Equation 3 gives the most accurate results, since it does not involve an exact knowledge of the weight in solution of either the comparison or the isotopic acid, but only a precise value for the increase in weight. The thermostat should be regulated to 0.001° or better, and the pycnometer should consist of a large spherical bulb with a short but very narrow neck graduated with a very fine line at its narrowest point. Above the neck is a bulb large enough to hold any solution which rises through the neck on account of thermal expansion. This is fitted with a very close fitting ground-glass stopper, and with very fine tubes for filling and emptying.

While the above procedure is the simpler from the standpoint of the equations involved, it happens that another method is more economical of time and material, so what has actually been done in most of the cases is to adjust the comparison and the isotopic acids to the same density, and to determine the number of molecules of hydrogen chloride, and therefore the number of atoms of chlorine, present by titration. In this case the acid in the pycnometer has a higher molecular concentration when the comparison acid is used. Very accurate density determinations have been made on solutions of very pure ordinary hydrochloric acid by Dull in this laboratory. From his data it may be calculated that the "apparent density" of hydrogen chloride in 5.91 N hydrogen chloride is 1.785, in 5.79 N it is 1.7852, while in 5.20 N it is 1.787, and in 2.315 N it is 1.856.

The difference in the titration values of the comparison and the isotopic acids may easily be calculated in the following way for any desired increase in the atomic weight ($-\Delta A$) of chlorine. Calculate the increase of weight which would occur if the comparison acid in the pycnometer were to be replaced by isotopic acid of the same titration value. Then calculate the number of equivalents of hydrogen chloride in the isotopic acid which must be replaced by water of a density 0.997077 (or 0.99604 as weighed by brass weights in air, if the temperature of the thermostat is 25°) in order to reduce its weight by the above difference. This gives the difference in the titration values of the two solutions when adjusted to the same density, which will be given directly in terms of 0.01 N sodium hydroxide solution, since the titration was completed with a base of this concentration, though begun with 1 N solution.

$$\Delta T = \frac{V.\ N \Delta A}{1000.\ M_c} \cdot \frac{\text{dHCl}}{\text{dHCl} - \text{dH}_2\text{O}} \cdot \frac{1}{10^{-5}} \tag{4}$$

or

$$\Delta A = 100 . \Delta T \ . \frac{\text{dHCl} - \text{dH}_2\text{O}}{\text{dHCl}} \cdot \frac{M_c}{V.N} . \tag{5}$$

Here the symbols have the same meaning as before, except that the following new ones are employed: M_c is the equivalent weight of hydrogen chloride in the comparison acid, and equals 36.468 in the present experiments; N is the normality of the comparison acid; dHCl is the apparent density of hydrogen chloride in the comparison acid; dH_2O is the density of water at the same temperature; ΔT is the difference in grams of $^1/_{100}$ weight normal sodium hydroxide between the pycnometer full of the two acids; 10^{-5} is the number of equivalents of sodium hydroxide in 1 c.c. of 0.01 N base. V is the volume of pycnometer in c.c. If V c.c. is titrated, the right-hand side of the Equation (5) for ΔA should evidently be multiplied by V/v.

Let T'_c and T'_i represent the titration values of the comparison and isotopic solutions in terms of normal solutions, then it is evident that Equation 5 may be given the following form:

$$\Delta A = \left(\frac{T_c}{T_i} - 1\right) \frac{\text{dHCl} - \text{dH}_2\text{O}}{\text{dHCl}} \cdot M_c \tag{6}$$

Method of Adjusting the Densities of the Isotopic and Comparison Acids.—After a preliminary determination of the densities of the two solutions, the concentration of the solution was read from a graph giving concentrations in terms of the density of ordinary pure hydrogen chloride, and from these values the amount of water necessary to decrease the concentration of the more concentrated solution to that of the more dilute was calculated. This first adjustment brought the densities of the solutions sufficiently close so that a difference of 5 or 6 mg. was all that remained for a volume equal to that of the pycnometer.

A second dilution was made by adding water up to the exact amount called for by the equation $(\mathrm{d}_1\mathrm{d}_2 - \mathrm{d}_2).W_w = W_s(d_2d_1)$, where d_1 is the smaller, and d_2 the larger density, W_w is the weight of water to be added to the weight W_s of the more dense solution in order to make the densities the same. This equation is not exact, since it takes no account of the volume change produced in adding water to approximately 6 *N* acid, so it does not bring the two weights closer together than 0.6 mg. An exact equation could easily be developed, but even with the form used only 0.2 g. of water had to be added to 75 g. of solution in the third dilution.

Error of Filling.—The pycnometer could be filled repeatedly with a *maximum* variation of 0.0012 per cent., while the usual error was considerably less. The thermostat was constant to within less than 0.001°.

Method of Titration.—First a series of indicator standards was made up in 125 c.c. tightly glass-stoppered Erlenmeyer flasks.[81] In each of these was put the same volume of conductivity water and the same amount of methyl orange as was used in the titrations. To these were added in order 0, 2, 4, and 6 drops of 0.01 *N* hydrochloric acid. The titrations were ended at a color between that in the two-drop and the four-drop flasks, and in good daylight the effect of one drop of 0.01 *N* base could be readily detected. A 1 *N* solution of sodium hydroxide was used to carry the titration to within one drop of the end-point, when it was finished with 0.01 *N* solution of the same base. Weight burets of 60 g. capacity were used and these were weighed on a balance sensitive to 0.02 mg. It was found that the use of a heavy " vacuum " stopcock grease completely stopped all loss of weight of the burets due to evaporation of the solutions through the ground-glass stopcocks.

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[81] Flasks with very narrow necks will be used for all future work, so that the evaporation may be decreased.

The samples for titration were weighed by measuring 5 c.c. of the 6 *N* solution, dropping it into the flask, and then determining the weight on the same balance as that used for the pycnometer. The ground-glass stoppers in the sample flasks were kept dry during the whole determination.

60. PURIFICATION OF ACID.

The acid used in the analyses as the reference or comparison acid was the light fraction from the first diffusion. A calculation showed that its atomic weight could not have been changed sufficiently to be detectable, and the process used would result in a considerable purification. The acid was treated with potassium permanganate and boiled to expel any iodine, bromine, or chlorine liberated, and was then distilled, rejecting the first third and the last one-fourth.

The isotopic acid was purified in several ways. As has been stated it was formed by the action of very pure sulfuric upon C. P. hydrochloric acid. The gas came in contact with only carefully cleaned and dried glass and porous porcelain, and was absorbed in conductivity water. After the second diffusion the salt formed by neutralizing the acid by very pure sodium hydrogen carbonate was recrystallized three times from pure water and was very thoroughly drained and washed with pure water each time. The mother liquor from these crystallizations showed no trace of iodine by the use of a test which would detect one part of iodine as iodide in twenty thousand parts of sodium chloride, as determined by repeated tests. This test consisted in the use of nitrosyl sulfuric acid and carbon disulfide with the proper precautions. Neither could bromine be detected in these mother liquors, but we did not rely upon this fact to insure the absence of bromine. In addition to these three crystallizations, the acid, after the third diffusion, was treated with potassium permanganate and distilled, using exactly the method employed with the comparison acid, except that the first and last fourths were rejected and the middle half was saved. Additional purifications were made by precipitation of sodium chloride from aqueous solution by the addition of isotopic hydrogen chloride. The sodium hydroxide used in the analyses gave no test for bromine. It was converted into sodium chloride and recrystallized, and the mother liquor again gave no test for bromine.

However, after the sodium hydroxide was added to any sample the latter was always purified carefully. Still further careful purifications were employed, as described in another paper,[82] but what is given above will be sufficient for inclusion here.

61. ANALYSIS OF THE PURIFIED THIRD DIFFUSION RESIDUE (Cut = 12,000).

In order that the magnitude of the errors involved may be realized the actual data for some of the analyses will be presented. First the reference acid and the isotopic acid were adjusted to practically the same density in a Harkins' pycnometer of about 22 c.c. volume. The weights were as follows:

TABLE XXXVIII B.

Analyses.

	First Series.		Second Series (after another distillation).	
	Weight *in vacuo* of pycnometer plus.			
	Reference acid.	Isotopic acid. ($t \pm 25° \pm 0.0005°$)	Reference acid.	Isotopic acid.
1.	37.2533	37.2530	37.2100	37.2095
2.	37.2535	37.2527	37.2100	37.2098
Av.	37.2534	37.25285	37.2100	37.20965
Diff.	0.00055 g. = 0.00148%		0.00045 g. = 0.00121%	

TABLE XXXVIII C.

Data on the Atomic Weight Determinations.

(Note that the two columns on the left of the table refer to one set of analyses, the two on the right to a second series.)

	First Series.	Second Series.
No. of mols. of HCl in 100 g. of sol.; from density.	$N = 5.91$	$N = 5.79$
Density of Isotopic Acid.	1.10195	1.00983

Bar. Pressure = 748.4 mm. ($h = 7.17$)* to 746.5 mm. ($h = 10.4$). $t = 24°$ to 26°.

Wt. of pycnometer of water.	35.0350
Wt. of pycnometer.	13.2765

* The absolute humidity in mm. of mercury is represented by *h*.

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[82] Harkins and Hayes: *J. Am. Chem. Soc.*, 43, page 1822 (1921).

Data for the Titration of the Reference and Isotopic Acids.†

NaOH used per 5 g. of acid.

	First Series.		Second Series.	
	26.2613	26.1970	25.7887	25.7173
	26.2669	26.2004	25.7848	25.7188
				25.7120
Av.	26.2641	26.1987	25.7867	25.7160
Diff. (g. of 0.01 N NaOH)	6.54			7.07
		After standing for one day.		
	26.2630	26.2030	25.7755	25.7094
	26.2673	26.2069	25.7745	25.7064
		26.2030	25.7752	
Av.	26.2651	26.2043	25.7751	25.7079
Diff. (g. of 0.01 N NaOH)	6.08			6.72
		After standing for two days.		
			25.7695	25.7045
			25.7671	25.7002
		Av.	25.7688	25.7023
Diff. (g. of 0.01 N NaOH)				6.65

Increase of Atomic Weight.

	First Series.			Second Series.		
	Uncorr.	Correction for density.	At. wt. increase.	Uncorr.	Correction for density.	At. wt. increase.
1st set.	0.0356	−0.0018	0.0338	0.0393	0.0016	0.0377
2nd set.	0.0331	−0.0017	0.0312	0.0374	0.0015	0.0359
3rd set.				0.0370	0.0016	0.0354
Av. increase in at. wt.			0.0325			0.0363
Average of Series 1 and 2			0.0344			

100 g. of chlorine obtained of atomic weight 35.494.

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† The weights of base and acid used in these titrations are reduced to the same barometric pressure and the same humidity for each series.

The corrections of about 0.0018 for the results of the first, and of 0.0016 for the results of the second series were calculated from the density differences by means of the same equation as was used for the calculation of the results of the titrations.

The difference between the averages of the atomic weights for the first and second series of analyses is 0.0038 unit of atomic weight which is very near the possible error in the atomic weight of chlorine according to Richards. While the data given indicate that the comparison method described is a very accurate one for the determination of the atomic weight of an isotope of chlorine, our experience has shown that its precision may be increased, provided as large quantities of acid are available, by the observance of certain precautions which may be introduced. The atomic weight of the chlorine produced by diffusion by the writers is very close to 35.494, while that obtained by Harkins and Broeker was 35.515. However, the amount of material produced by the present work is very much greater.

62. REPURIFIED FOURTH DIFFUSION RESIDUE (Cut = 240,000).

The hydrochloric acid obtained from the third diffusion had been converted largely into sodium chloride in the titrations on the third diffusion residue, so the remaining acid was neutralized with sodium hydrogen carbonate. The salt thus obtained was converted into hydrogen chloride, and again diffused. The hydrochloric acid thus obtained was distilled fractionally, after heating with potassium permanganate. The middle portion was used for the analyses reported below.

TABLE XXXIX.

Analyses.

	Reference acid.	Weight *in vacuo* of pycnometer plus (t. 25° + 0.0005).	Isotopic acid.
1.	36.4461		36.4465
2.	36.4460		36.4465
Av.	36.44605	Diff. 0.00045	36.4465

No. mols. in 1000 g. solution from density.	Density of isotopic acid.
$N = 5.22$	$d^{25} = 1.08868$

Barometric pressure = 737 to 739 mm. Absolute humidity = 7.6 to 7.05 mm.
Temperature = 24 to 26°.

Data for the Titration of the Reference and Isotopic Acids.
(All weights corrected to 737 mm. and $h = 7.6$.)

N NaOH per 5 g. of acid.

First Day.

Reference acid.	Isotopic acid.
G.	G.
23.3430	23.2898
23.3456	23.2870
23.3443	23.2884

Diff. 5.59 g. of 0.01 N NaOH.

Second Day.

23.3359	23.2793
23.3401	23.2785
23.3369	23.2755
23.3376	23.2778

Diff. 5.98 g. of 0.01 N NaOH.

Increase in Atomic Weight above 35.46.

	Uncorr.	Correction for density.	Atomic weight increase.
1st day's determinations	0.0346	Add. 0.0017	0.0363
2nd day's determinations	0.0370	0.0017	0.0387
		Av.	0.0375

Nine g. of chlorine as hydrogen chloride of atomic weight 35.498 were obtained in this diffusion. The fourth diffusion was not so efficient as the first three, since the apparatus is better designed for larger samples, and in this diffusion the gas passed through only a short length of porous tube of large diameter.

63. APPLICATION OF THE ELEMENTARY THEORY OF DIFFUSION TO THE SEPARATION OF ISOTOPES BY DIFFUSION OR BY AN IRREVERSIBLE EVAPORATION.

One of the most simply derived of all of the relations of the kinetic theory of gases is that which states that the mean velocity of the molecules of a gas varies inversely as the square root of the molecular weight. Upon the basis of this relation Lord Rayleigh[83] in 1896 developed an equation which makes it possible to calculate the enrichment of a diffusion residue with respect to the heavier molecules in a mixture of *two gases,* as the cut increases. The cut may be defined as the number of mols of the initial mixture which have given 1 mol of the heavy fraction in question. Table XL illustrates the change of atomic weight of neon and of chlorine with the cut.

This table indicates that it is easier to secure a change of 0.1 unit in the atomic weight of chlorine than in that of neon, if the cut alone is taken into account. The conditions are also more favorable to the chlorine from the point of view of abundance, ease of handling, and ease of purification. It will be seen that to secure 10 grams of chlorine with this increase of atomic weight, it would be necessary to start with 186 kilos of chlorine in the form of hydrogen chloride, provided the intermediate fractions are not refractionated. This involves the assumption that the efficiency of the process is kept equal to 100 per cent., which is by no means easy.

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[83] *Phil. Mag.* (5), **42**, 493 (1896).

TABLE XL.

Values of the Cut $(X + Y) / (x + y)$ *Necessary for Increase of the Atomic Weights of Chlorine and of Neon by Definite Amounts. A Diffusion of the Heavy Fraction. (Chlorine diffused as hydrogen chloride.)*

(Percentage of isotope of atomic weight 37 in chlorine = 23, of atomic weight 22 in neon = 10.)

	Chlorine.		Neon.	
Increase of atomic weight.	Cut.	Corresponding enrichment.	Cut.	Corresponding enrichment.
0.05	160	1.1459	217	1.286
0.10	18,600	1.302	19,600	1.588
0.15	1,690,000	1.469	991,000	1.909
0.20	117,000,000	1.648	33,000,000	2.25

Mulliken and Harkins,[84] in a paper from which much of the following material has been taken, have developed equations which bring to light the various factors involved in the separation. Their more complete equations give the enrichment of the light, as well as the heavy fraction, and also apply to a mixture of any number of isotopes. On account of the more general applicability of their equations the discussion given in the present paper will be based on their system of treatment.

Almost the only discussion, other than our own, of the application of the theory of gaseous diffusion to the separation of isotopes, has been given by Lindemann and Aston,[85] and by Aston,[86] on the basis of the *equation of Rayleigh*. In these discussions too much weight has been placed on the diffusion exponent, and too little on the composition of the isotopic mixture which constitutes what we know as the element. Thus Aston (*loc. cit.*) states that the most favorable case known for the separation of isotopes is that of neon, since only the 21st root is involved as the diffusion exponent.

What is the most favorable case depends not only upon the facts, but upon the point of view. Thus the aim of the work may be to attain:

1. The greatest possible difference of relative density.
2. The greatest possible difference of atomic weight.
3. The most complete separation of the isotopes.

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[84] *J. Am. Chem. Soc.*, 44, 37–65 (1922).

[85] *Phil. Mag.*, 37, 53 (1919).

[86] "Isotopes," p. 130.

It is obvious that these are not the only factors, since the amount of material obtained (number of mols) is also of prime interest.

It is easy to show that for a mixture of two isotopes the *rate of separation* is as follows:

A.	*B.*
In Terms of Relative Density.	*In Terms of Change of Atomic Weight.*

1. Proportional to the square of the interval between the molecular weights.
2. Proportional to the product of the mol-fractions of the isotopes.
3. Proportional to the logarithm of the cut.

4A. Inversely proportional to the *square* of the ordinary molecular weight.	4B. Inversely proportional to the ordinary molecular weight.

It will be seen that *only the fourth factor is different in the two cases. For a given element the rate of separation in either sense is inversely proportional to the molecular weight of the compound in which the element is combined.* The second factor listed above indicates *that the most favorable mixture for the separation of two given isotopes is that which consists of fifty (molar) per cent. of each.*

The increase in molecular weight (ΔM) is given approximately by the following simple equation:

$$\triangle M = \frac{(M_2 - M_1)^2 x_1 x_2}{M_2} \ln C = B \ln C$$

in which M_1 and M_2 are the molecular weights of the light and heavy isotopes, respectively, x_1 and x_2 are the corresponding mol fractions, and C is the cut. B, which is aproximately constant, is the *separation coefficient,* with respect to the molecular weight. *The rates of separation of the isotopes of various elements are proportional to the corresponding values of B.*

64. THE RATE OF SEPARATION OF VARIOUS NATURAL ISOTOPIC MIXTURES.

The relative rates of separation of all of the elements whose isotopic composition is known quantitatively are shown by Table XLI, in the form of the separation coefficient B, which gives also the absolute rate of separation. *This table is of great value, since it is the first to give this important information.*

If, for example, neon and hydrogen chloride are compared, it is found that the latter has the higher separation coefficient. If the approximate equation given above is considered, it is seen that $(M_2 - M_1)^2$ is the same for both of these elements, while the molecular weights give a factor of $\frac{36.46}{20.20}$ or 1.805 in favor of the neon. However, the product of the mol fractions is 0.0900 for neon and 0.1771 for hydrogen chloride, thus giving a factor equal to 1.970 in favor of hydrogen chloride. Though the initial diffusion coefficient is thus more favorable in the case of hydrogen chloride, if an extensive series of diffusions is carried out, it is found that in the case of the *heavy fraction* the diffusion coefficient for both substances increases as the diffusion proceeds, but much more rapidly for neon, so the diffusion coefficient of the latter soon becomes the larger. However, with the *light fraction* the diffusion coefficients of both become less favorable, and that of neon becomes less favorable even more rapidly than that of hydrogen chloride.

TABLE XLI.

Composition and Separation Coefficients of Isotopic Mixtures.

Element of compound.	At. wt. or mol. wt.	At. or mol. wts. of isotopes.	Corresponding mol-percentages.	$1-k^{1}_{2}$	B or B'/n_e	E or E'/n_e
Li	6.94	6,7	6,94	0.0742	0.00450	0.00403
B	10.9	10,11	10,90	0.0466	0.00438	0.00409
BH_3	13.9	13,14	10,90	0.0364	0.00339	0.00322
Ne	20.2	20,22	90,10	0.0466	0.00843	0.00818
Mg	24.32	24,25,26	79,10,11(?)	......	0.00868	0.00843
HCl	36.46	36,38	77,23	0.02668	0.00950	0.00932
CH_3Cl	50.46	50,52	77,23	0.01941	0.00690	0.00681
Cl_2	70.92	70,72,74	59 .3,35 .4,5 .3	......	0.00494	0.00499
CH_2Cl_2	84.92	84,86,88	59 .3,35 .4,5 .3	......	0.00413	0.00417
$CHCl_3$	119.38	118,120,122,124	4.7,40 .9,12 .2,1 .2	......	0.00295	0.00296
CCl_4	153.84	152,154,156,158, 160	35 .2,42 .0,18 .8,3 .7,0 .3	......	0.00229	0.00231
Ni	58.68	58,60	66,34	0.01680	0.00758	0.00747
$Ni(CO)_4$	170.68	170,172	66,34	0.00582	0.00262	0.00260
Zn	65.37	64,66,68,70	51 .5,31,15,2 .5(?)	......	......	0.02037*
K	39.10	39,41	95,5	......	......	0.00232
Rb	85.45	85,87	77 .5,22 .5	......	......	0.00409
Kr	82.92	78,80,82,83,84,86	6,15,18,16,25,30	......	......	0.0306
HBr	80.92	80,82	54,46	0.01228	0.00614	0.00606
Hg	200.6	197–200,202,204	....	......	0.0063	(experimental)†

* These values of E are practically the same as the values of B in the cases of Zn, Rb, and Kr. E is the separation coefficient calculated from a less exact equation than that used in the calculation of B. The meaning of the column $1 - k^{1}_{2}$ may be found in the later sections of the paper in which the equations involving B and E are devoloped.

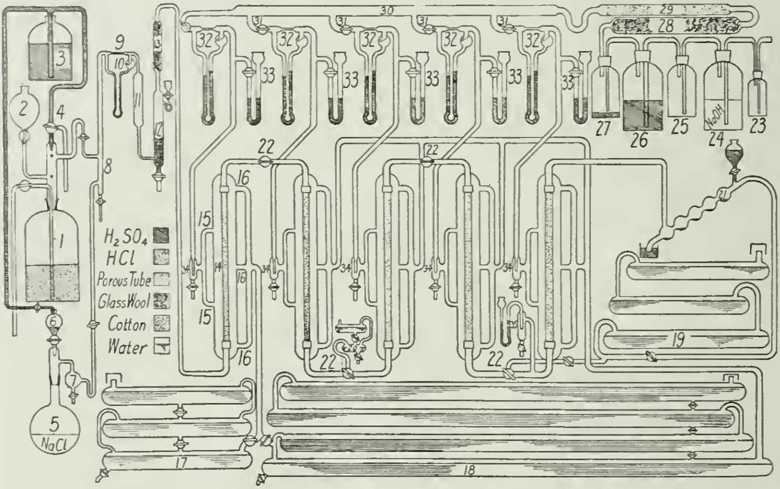
† The value 0.0063 for the separation coefficient of mercury was determined by ***diffusion*** at low pressures through a membrane of filter paper. The highest separation obtained by the method of vaporization at low pressure corresponds to a value for the coefficient of 0.0057.

The compounds of chlorine listed in the table indicate that if Cl, Cl_2, Cl_3, and Cl_4 could be diffused, the relative rates of separation in terms of the change of atomic weight (separation coefficient) would be, respectively, 1, $^1/_2$, $^1/_3$, and $^1/_4$. The values given in the table are slightly different from what would be expected from these ratios, since all but Cl_2 are loaded with either hydrogen or carbon.

The highest rate of separation for an *element* of given isotopic composition is that for monatomic molecules of the pure element.

The separation coefficient B/n_e is very nearly inversely proportional to the total molecular weight (see table), whether the molecule contains one or more atoms of the isotopic element. When n_e, that is, the number of atoms of the isotopic element (*i.e.*, 4 in CCl_4), is greater than 1, the presence of different isotopes in a single molecule tends to reduce the separation coefficients, as pointed out in connection with molecular chlorine. This is, however, balanced by the effect of the large difference in molecular weight of the lightest and heaviest molecular isotopes, so that the effect of the total molecular weight, as indicated by Equations 7A and 7A′ given later, is alone effective. For the separation of the element chlorine, hydrogen chloride is evidently the most favorable compound. The separation coefficient of mercury is rather low, but this is more than compensated, from the experimental standpoint, by the chemical inactivity, volatility and ease of purification of the element, and the accuracy with which changes in atomic weight can be determined by density measurements. According to the theory of Harkins,[87] many or most of the *even-numbered elements* above nickel should contain numerous isotopes. In agreement with this, Aston has found 6 or 7 isotopes each for the elements krypton, xenon, and mercury, and 8 for tin. The wide separation of the extreme atomic weights tends to give

FIG. 29.



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[87] *J. Am. Chem. Soc.*, 37, 1367 (1915).

such elements a large separation coefficient, if the extreme components are present in any considerable proportion, for the coefficient depends on the *squares* of the intervals in atomic weight between isotopes (see Equation 7A′).

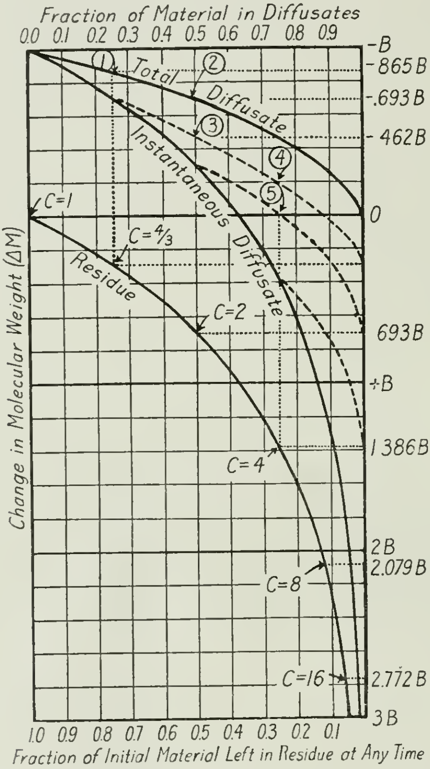
Such elements as selenium, cadmium, tin, and tellurium, should, on this basis, and in the absence of specific information as to the isotopic composition, be favorable cases for separation. Experiments upon zinc and cadmium have been begun in this laboratory.

For elements or compounds containing more than two isotopes, it is possible to calculate from the coefficient E a virtual atomic or molecular weight interval $(\Delta M)_v$ corresponding to the case of only two isotopes. For example, the mixture of isotopes in mercury is equivalent to an equimolal mixture of two isotopes having an atomic weight difference of 3.15 units. This is obtained by putting $\frac{(\Delta M)^2 x_1 x_2}{2M} = E = 0.0063$, setting $x_1 = x_2 = 0.50$, and solving for ΔM: $(\Delta M)_v = \sqrt{8EM}$. For magnesium, $(\Delta M)_v = 1.32$; for hydrogen chloride, 1.68; for chlorine, 2.44; for carbon tetrachloride, 3.4; for zinc, 3.3, etc.

The progress of a separation of any number of isotopes can be predicted very closely by the use of Fig. 30, which relates to a process whose efficiency is 100 per cent. This figure indicates that at the beginning of a diffusion process, or of an irreversible evaporation, the diffusate has a molecular weight which is B units less than that of the mixture, and is thus 0.020 unit lighter for zinc, 0.00932 unit lighter for HCl, 0.0063 unit lighter for mercury, etc. The composition of the diffusate leaving when the residue contains about 37 per cent. of the material, is the same as that of the initial material, and the density of the diffused material increases above that of the initial substance as the mass of the residue decreases beyond this value (curve for the "Instantaneous Diffusate"). When the cut has reached 16, that is when 1/16 of the original material is in the residue, the atomic weight of the residue or heavy fraction is 2.77 B units higher, and that of the instantaneous diffusate being collected (light fraction) is 1.77 B units higher than the initial atomic weight.

It is of considerable importance in the experimental separation to keep in mind that the curve for the instantaneous diffusate is such that the molecular weight of the diffusate is always just B units less than that of the residue. However, it should be noted that B is not actually constant, but that it changes slowly as the separation proceeds. Thus the separation coefficients (B) for neon and hydrogen chloride increase as the separation proceeds, while that for lithium decreases. When more than two isotopes are involved the variation of the separation coefficient is less simple, but may be easily calculated in each specific instance.

FIG. 30.



Generalized plot showing atomic or molecular weight of fractions obtained during a 100 per cent. efficient diffusion or irreversible evaporation of a mixture of isotopes.

The curves are based on Equations 7, 12, and 16, of the text. The ordinates are expressed in terms of the "separation coefficient" B as a unit; this has a different numerical value (usually about 0.003 to 0.02) for each element (see Table I, and text). The value of B changes slightly with ΔM. The symbol C stands for the "cut" or *ratio* of quantity of material in the *residue* at any time to the *initial* quantity; for any abscissa on the lower scale, the "cut" is merely the reciprocal quantity. The "instantaneous diffusate" curve gives at any point the composition of the material which is at any instant diffusing or evaporating from residual material corresponding to the same abscissa. Note that this curve has exactly the same form as the residue curve, and differs only in an upward displacement of the ordinates by B units. Each point on the "total diffusate" curve gives the average composition of the material which has diffused or evaporated from the beginning up to that point. The various dotted curves give the composition of *fractions* of the total diffusate beginning at various points *after the beginning of the operation.* The meaning of the total diffusate curves can be made clearer by a few examples. Thus, Point I gives the composition of the diffused or condensed fraction for the interval 0–25 per cent.; Point 2, for the interval 0–50 per cent.; 3, for 25–50 per cent.; 4, for 25–75 per cent.; 5, for 50–75 per cent. Taken in connection with the residue curve, the total diffusate curves show how the original material can be divided efficiently into isotopic fractions. For example, the curves show that the diffusate might be collected in fractions as follows: 0–25 per cent., $\Delta M = -0.865B$; 25–50 per cent., $\Delta M = -0.462B$; 50–75 per cent., $\Delta M = 0$. If the operation were stopped here, the residue would have the atomic or molecular weight $M + 1.386B$, if M is the original atomic or molecular weight.

65. EQUATIONS FOR THE SEPARATION OF ISOTOPES BY DIFFUSION AND EVAPORATION.

It seems of value to collect here the simpler equations, to be developed later in this paper, which refer to the separation of isotopes by diffusion, irreversible evaporation, thermal diffusion, or centrifuging. The numbers of the equations are the same as are used in the later development.

For a mixture of two isotopes, the equations for the residue in an evaporation or diffusion process are

$$\triangle x_2 = \frac{(1-k)x_1x_2}{2(x_1+kx_2)} \cdot \ln C = A \ln C \qquad (6)$$

$$\text{or, approximately, } \triangle x_2 = \frac{(M_2 - M_1)\, x_1x_2}{2M} \cdot \ln C \qquad (6A)$$

$$\text{and } \triangle M = A(M_2 - M_1) \ln C = B \ln C \qquad (7)$$

$$\text{or approximately, } \triangle M = \frac{(M_2 - M_1)^2 x_1x_2}{2M} \cdot \ln C \qquad (7A)$$

Similar relations hold for a mixture of any number of isotopes. The x's denote mol-fractions, the M's atomic or molecular weights; $K = \sqrt{M_1/M_2}$; and C, the "cut," is the ratio of the initial to the final number of mols present in the residue.[88] The subscript 1 refers to the lighter, 2 to the heavier isotope. M without a subscript stands for the ordinary, average, atomic or molecular weight. B is called the separation coefficient. For the diffused or evaporated material, the equations are $-\Delta x_2 = A \ln \frac{C}{C-1}$ (15), and $-\Delta M = B \ln \frac{C}{C-1}$ (16). The *total difference* in atomic weight between the two fractions is then

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[88] In the case of gaseous diffusion, the numerical factor in the denominator is not necessarily 2, but probably is close to 2, in most cases; the same applies to the exponent c in the value of k; *in general* $k = \sqrt[c]{M_1/M_2}$

$$\triangle\triangle M = \triangle M - (-\triangle M) = [B + B/(C-1)] \ln C = B.\ C.\ \ln \frac{C}{C-1} \qquad (19)$$

$$= \frac{(M_2 - M_1)^2 x_1 x_2}{2M} \cdot \frac{C}{C-1} \cdot \ln C, \text{ nearly.} \qquad (19A)$$

For $C = 1$, $\triangle\triangle M = B$; for $C = 2$, $\triangle\triangle M = 2B \ln 2 = 1.386\,B$;
for $C = 4$, $\triangle\triangle M = (8/3)\,B \ln 2 = 1.848\,B$; etc.

The value for $C = 2$ is of the most interest, since it corresponds to a division of the material into two equal fractions. A convenient equation for use with *intermediate fractions* is

$$\triangle M = \frac{B}{C_2 - C_1}(C_1 \ln C_2 - C_2 \ln C_1).$$

Chapman's equation for *thermal diffusion* may be changed into a form which is similar, as follows:

$$\triangle M = K.B \ln \frac{T'}{T} \qquad (21)$$

in which B has its usual value. Since K is about ¼, thermal diffusion, for any ordinary ratio of temperatures such as $\frac{1240°}{80}$, is a much weaker agent than ordinary diffusion, since this ratio causes only half the change of molecular weight for a cut of 2 as is given by the same cut when the latter method is used.

For *pressure diffusion,* such as that due to centrifugal force,

$$\triangle M = B \ln \frac{p}{p_0} \text{ (approximately).} \qquad (27)$$

or

$$\triangle M = \frac{(M_2 - M_1)^2 x_1 x_2}{2RT}(v^2 - v_0^2) = P(v^2 - v_0^2) = Pw^2(r^2 - r_0^2) \qquad (28)$$

The equations for thermal and pressure diffusion, as given above, were developed in this laboratory by Mulliken.[89] Rayleigh's equation (1) was developed for the calculation of the diffusion of gases into each other, but it may be easily shown that it is also applicable to irreversible evaporation. Let x and y represent the number of mols of the light and heavy isotope, respectively, in the *heavy fraction* after the diffusion, and X and Y the initial mol numbers. Then

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[89] *J. Am. Chem. Soc.*, 44, 1033–51 (1922).

$$\frac{1}{C}=\frac{x+y}{X+Y}=\frac{X}{X+Y}r^{\frac{\mu}{v-\mu}}+\frac{Y}{X+Y}r^{\frac{\mu}{v-v}} \tag{1}$$

where μ and v represent the diffusion coefficients of the light and heavy constituents, respectively. This is easily converted into the form

$$\frac{Q}{Q_0}=\frac{1}{C}=r^{\frac{v}{v-\mu}\left[1+\frac{Y}{X+Y}(r-1)\right]} \tag{2}$$

If it is assumed that the rates of diffusion of the gases vary inversely as the square roots of their molecular weights, this reduces to the following simple form:

$$\frac{1}{C}=r^{\frac{\sqrt{M_h}}{\sqrt{M_l}-\sqrt{M_h}}\left[1+h_0(r-1)\right]} \tag{3}$$

in which h_0 represents the fraction of the heavy isotope $Y/(X+Y)$ in the initial mixture, and M_l and M_h are the molecular weights of the light and heavy components of the mixture.

66. RELATION BETWEEN THE ATOMIC WEIGHTS AND PERCENTAGES OF TWO ISOTOPES AND THE ATOMIC WEIGHT OF THE MIXTURE.

In order to calculate the cut necessary to produce a certain change in the atomic weight of a mixture of two isotopes, it is necessary to know the fraction of each in the mixture, and this may be calculated from the mean atomic weight and the atomic weights of the pure isotopes. Let h_0 and l_0 represent the initial fractions of the heavy and light isotopes, h and l the similar values necessary to produce the required enrichment (r), and M, M_h, and M_l, the molecular weights of the mixture, of the heavy, and of the light fractions.

Then

$$l\,.\,M_l+(1-l)\,M_h=M$$

or

$$l=(M_h-M)\,/\,(M_h-M_l). \tag{4}$$

Similarly

$$(1-h)\,M_l+h\,M_h=M$$

or

$$h=(M-M_l)\,/\,(M_h-M_l). \tag{5}$$

Divide (4) by (5):

$$r=\frac{h/l}{h_0/l_0}=\frac{M-M_l}{M_h-M}\cdot\frac{M_h-M_0}{M_0-M_l}. \tag{6}$$

By the use of Equations 3 and 6 the calculation of the cut necessary to produce any possible desired increase in atomic weight is very simple. It is obvious that the two equations may be combined into one.

$$\frac{Q_\circ}{Q} = \frac{1}{C} = \left[\frac{M-M_l}{M_h-M} \cdot \frac{M_h-M_\circ}{M_\circ-M}\right]^{\frac{\sqrt{M_h}}{\sqrt{M_l}-\sqrt{M_h}}} \left[1+h_\circ\left(\frac{M-M_l}{M_h-M} \cdot \frac{M_h-M_\circ}{M_\circ-M}-1\right)\right]. \tag{7}$$

If we let k represent $\frac{\sqrt{M_h}}{\sqrt{M_l}-\sqrt{M_h}}$ the "diffusion exponent," then the diffusion equation reduces to the simple form:

$$\frac{1}{C} = [1 + h_\circ (r-1)] \times r^k. \tag{8}$$

The value of the diffusion exponent (k) as thus defined is –37.503 for the isotopic forms of hydrogen chloride provided the only isotopes have molecular weights 36.008 and 38.008, while for neon it has the value –21.488, provided the only isotopes have atomic weights 20 and 22. It may be noted that the values of the diffusion exponents are not very different from the mean molecular weights, but that this is not a general relation unless the isotopes differ in atomic weight by 2, is shown by the fact that the exponent for lithium, with atomic weights 6 and 7, is –13.48. The exponent for the isotopic forms of hydrogen bromide of molecular weights 80 and 82 (bromine of atomic weights 79 and 81) is –81.492. A convenient rule for keeping in mind the magnitude of the exponent is that it has a value equal to half a unit more than the mean of the molecular weights of the isotopes when the two molecular weights differ by 2. Thus for isotopes of atomic weights 223 and 225, the exponent is –224.5. Obviously the exponent has larger values when the difference between the isotopes is only 1, and smaller values when it is greater than 2. When the difference is 1 the exponent is equal to half a unit more than *twice* the mean of the atomic weights, and when it is 4, it is equal to half a unit more than *one-half* the mean.

Equation 8 may be put in the form

$$\frac{1}{C} = \left[1 + l_\circ (r-1)\right] \times r^{k+1} \tag{9}$$

or
$$\frac{1}{C} = r^{\frac{\sqrt{M_l}}{\sqrt{M_l}-\sqrt{M_h}}}\left[1 + l_\circ (r-1)\right] = r^{k'}\left[1 + l_\circ (r-1)\right]. \qquad (10)$$

The numerical value of k' is always one unit less than that for k, and the mean of these two values is for two isotopes equal to the mean of the molecular weights when the molecular weight difference is 2, twice the mean of the molecular weights when this difference is 1, and one-half the mean of the molecular weights when this difference is 4, or

$$\frac{k+k'}{2} = \frac{M_l + M_h}{M_l - M_h} \qquad (11)$$

and
$$k + k' = 1. \qquad (12)$$

67. ISOTOPIC MOLECULES AND ISOMERIC MOLECULAR ISOTOPES.

It is of considerable interest that the existence of isotopic atoms necessitates the existence of *isotopic molecules,* and that the number of the latter is very great. Thus zinc has 4 and chlorine has 2 known isotopes, which corresponds to the existence of 12 molecular isotopes of zinc chloride. Since tin has 8 isotopes, there are 40 molecular isotopes of $SnCl_4$. The number of isotopes of $SnBr_4$ is also 40, while for $SnBr_2Cl_2$ it is 72.

If an element containing mol-fractions x_1 and x_2 of two isotopes is combined into molecules containing n_e atoms each of this element, there will be $n_e + 1$ isotopic molecular species, whose mol fractions can be shown to be given by the successive terms of the expansion of $(x_1 + x_2)^{n_e}$. If the element has (s) instead of only two isotopes, the corresponding expression is $(x_1 + x_2 + \ldots + x_s)^{n_e}$, which gives $\frac{(n_e+s-1)!}{n_e!(s-1)!}$ terms, corresponding to an equal number of molecular isotopes. If the compound contains atoms of several elements $E, E', E'', \ldots$, each having a set of isotopes, as $E_1, E_2, \ldots E_s$, for element E; $E'_1, E'_2, \ldots E'_{s'}$, for element E', etc., and if each element contains mol-fractions $x_1, x_2 \ldots x_s$; $x'_1, x'_2, \ldots x'_s$, etc., of its isotopic atomic species, then the mol-fractions of the various possible molecular species will be given[90] by the terms of the complete expansion of $(x_1 + x_2 + \ldots\ldots x_s)^{n_e}\ (x'_1 + x'_2 + \ldots\ldots x'_{s'})^{n'_e}$ $(\ldots\ldots)\ (\ldots\ldots)\ldots$ The total number of terms, and so of molecular isotopes, is $\frac{(n_e+s-1)!(n'_e+s'-1)!(\ldots\ldots)!(\ldots\ldots)!\ldots}{n_e!n'_e!\ldots\ldots(s-1)!(s'-1)!(\ldots\ldots)(\ldots\ldots)}$. The composition of the molecular species to which any term refers is given by the particular x's occurring in that term, and their exponents. Thus $(x_1)\ (x_2)\ (x'_4)\ (x'_1)_2\ (x'_2)_4$ would be the mol-fraction of the molecular species $E_1E_2E'_4(E''_1)_2(E''_2)_4$. Since 2 isotopes each have been detected for chlorine and for bromine, and probably 6 for mercury, the number of isotopes of either $HgCl_2$ or $HgBr_2$, which accords with our present knowledge, is given by the expression $\frac{6!\quad 3!}{1!\quad 2!\quad 5!\quad 1!} = 18$. The corresponding expression for $NiCl_2$ or $NiBr_2$ is $\frac{2!\quad 3!}{1!\quad 2!\quad 1!\quad 1!} = 6$, since there are 2 isotopes of nickel.

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[90] These expressions take account of all elements present in a compound, even if some of them contain only one isotope ($s = 1$). The factor $\frac{(n_e+s-1)!}{n_e!(s-1)!}$ reduces to 1 in the latter case ($0! = 1$, by definition), so that it is necessary to consider only the elements in the molecule which contain isotopes.

Among compounds containing more than one isotopic element, there will often be instances of isotopes of equal molecular weight. For example, $MgCl_2$, under conditions[91] where its molecules exist as permanent entities, would contain 9 isotopes having molecular weights 94, 95, 96, 96, 97, 98, 98, 99, 100. For both $Mg^{24}Cl^{35}Cl^{37}$ and $Mg^{26}(Cl^{35})_2$ the molecular weight is 96, and for both $Mg^{24}(Cl^{37})_2$ and $Mg^{26}Cl^{35}Cl^{37}$ it is 98 (isobaric molecules).

When an isotopic element appears in an organic molecule, its isotopism not only results in numerous isotopic molecular species, but also in many cases introduces new position isomers. For example, C_6Cl_6 must have 7 molecular isotopes, of which all but $C_6(Cl^{35})_6$ and $C_6(Cl^{37})_6$ must exist in several isomeric forms, due to the presence of the two different substituents Cl^{35} and Cl^{37}. Again, $CH_3.CHCl.CH_2Cl$ must consist of 4 molecular species, the isotopes $CH_3.CHCl^{35}.CH_2Cl^{35}$, $CH_3.CHCl^{37}.CH_2Cl^{37}$, $CH_3.CHCl^{35}.CH_2Cl^{37}$, and $CH_3.CHCl^{37}.CH_2Cl^{35}$, the last two being isomeric forms of the same isotope.

New optical isomers are possible as a result of isotopism, if isotopic atoms, by virtue of their different *masses* alone, can act as different substituents to make carbon or other atoms asymmetric.

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[91] *I.e.*, in the vapor state, or in solution in non-ionizing solvents.

(To be continued.)

NOTES FROM THE U. S. BUREAU OF STANDARDS.*

A PIEZO ELECTRIC METHOD FOR THE INSTANTANEOUS MEASUREMENT OF HIGH PRESSURES.[1]

By J. C. Karcher.

[ABSTRACT.]

A NUMBER of circular quartz plates are cut from a quartz crystal so that an electric axis is perpendicular to the plane surface of the plates. These plates are stacked up condenser fashion with sheet metal electrodes. Electrodes collecting charges of like sign are connected to a common terminal. The two terminals are electrically connected to a ballistic galvanometer.

The stack of plates is subjected to the pressure to be measured by means of a piston which exerts a force perpendicular to the plane faces of the plates. When pressure is applied, a charge is liberated by the plates which flows through the galvanometer, causing a deflection. The galvanometer deflection is photographed on a rapidly-moving film. The pressure-time curve is the differential of the recorded deflection-time curve multiplied by the proper constant.

It has been found that the amount of charge liberated by the quartz plates is proportional to the pressure applied, for pressures up to 50,000 pounds per square inch. If the dynamic equation for the motion of the galvanometer is

$$Gi = K\frac{d^2\Theta}{dt^2} + D\frac{d\Theta}{dt} + U\Theta$$

where G is the dynamic constant of the moving system, K its moment of inertia, D the damping constant and U the restoring constant of the galvanometer. If the piezo electric current of the gage is C, then

$$\frac{dq}{dt} = C\frac{dP}{dt} = i.$$

If the time of duration "t" of the pressure phenomena is small compared to the period of the galvanometer, and if the

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* Communicated by the Director.

[1] *Scientific Papers,* No. 445.

amount of damping on the galvanometer is small, then U and D will be small and

$$GC\frac{dP}{dt} = K\frac{d^2\Theta}{dt}$$

$$P = \frac{K}{GC}\frac{d\Theta}{dt} + C' \left(P = O \text{ when } \frac{d\Theta}{dt} = U \therefore C' = 0\right)$$

$d\theta/dt$ is determined by reading slopes on the recorded deflection-time curve. K/GC is determined by calibrating the gage in a testing machine. The gage is subjected to a known load P_0 and the galvanometer deflections θ_0 is read, then

$$\frac{K}{GC} = \frac{P_0 T}{2\pi(1 + \lambda/2)\Theta_0}$$

where λ is the logarithmic decrement of the galvanometer. Computations are made to show the sensitivity of the system.

Actual pressure measurements in guns have been made with several gages. A comparison with other data obtained simultaneously indicates that the performance of the gage is in entire accord with the theory developed. Results are not available for publication.

SPECTROPHOTOELECTRICAL SENSITIVITY OF ARGENTITE (Ag_2S).[2]

By W. W. Coblents.

[ABSTRACT.]

The present paper, considered in connection with some previously published data, represents a study of the effect of crystal structure upon photoelectrical sensitivity, as observed in silver sulphide, Ag_2S, in the isometric form argentite, and in the orthorhombic form, acanthite.

Experimental data are given on the effect of temperature, of the intensity of the radiation stimulus, and of mechanical working of the material, upon the spectrophotoelectrical sensitivity of argentite. These observations are then compared with similar data, previously published, on acanthite.

Argentite reacts slightly photoelectrically to radiations of wave-lengths 0.5 to 1.1μ, followed by a sharp, fairly symmetrical maximum at 1.35μ. In contrast with this is acanthite, which reacts quite strongly to radiations at 0.5 to 1.0μ followed by an

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[2] *Scientific Papers*, No. 446.

unsymmetrical maximum at 1.35μ. Both minerals react selectively to ultra-violet rays.

At low temperatures, the intrinsic photoelectrical sensitivity of argentite is greatly increased and the maximum shifts to the short wave-lengths—to 1.1μ as compared with 1.2μ for acanthite, under similar conditions.

The photoelectrical reaction of argentite differs from that of acanthite in being free from an induced photonegative polarization.

In argentite, as previously observed in acanthite (also molybdenite, etc.), increasing the intensity of the radiation stimulus produces a more rapid reaction in the long wave-lengths than in the short wave-lengths, with a consequent shift of the maximum of the photoelectrical sensitivity curve toward the long wave-lengths.

Hammering the crystals of argentite and acanthite into thin. pliable, plates lowers the intrinsic photoelectrical sensitivity. The position of the maximum of spectrophotoelectrical sensitivity of the worked samples is less affected by changing the temperature than obtains in the natural crystalline state; and it is practically the same for these two minerals, at low temperatures. From this it appears that aside from the effect of crystal structure, silver sulphide has a photoelectrical response spectrum characteristic of this substance.

From a comparison of the spectrophotoelectrical reactions of these two crystal forms of silver sulphide under various conditions it appears permissible to conclude that crystal structure has a marked effect upon spectrophotoelectrical sensitivity.

THE DECARBURIZATION OF FERRO-CHROMIUM BY HYDROGEN.[3]

By Louis Jordan and F. E. Swindells.

[ABSTRACT.]

The recently developed "rustless" iron may be considered as a stainless steel from which the carbon has been largely eliminated. The carbon content of rustless iron is in the neighborhood of, or less than, 0.1 per cent. In order to produce an iron alloy containing as high as 12 per cent. chromium and still keep the carbon content as low as indicated, it is necessary to use ferro-chromium lower in carbon than the more common commercial grades bearing 4 to 8 per cent. carbon. Carbon-free ferro-chromium made by alumino-thermic methods is available, but at prices which are too high to allow its extended use in producing rustless iron.

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[3] *Scientific Papers,* No. 448.

Various procedures for decarburizing high-carbon ferro-chromium have been described in a number of patents. The decarburization of ferro-chromium by means of hydrogen has been suggested. The decarburization of cast iron and steels by heating in hydrogen at temperatures between 400° and 1200° C. has been described previously. Tests carried out on 60 per cent. ferro-chromium containing 8 per cent. carbon showed that there was a slow decarburization of the powdered ferro alloy by dry hydrogen between 1100° and 1350° C. The removal of carbon was more rapid just above than just below the melting point of the alloy. The most rapid decarburization was secured by bubbling hydrogen through molten ferro-chromium at approximately 1500° C. Under these conditions nearly 1 per cent. of carbon was removed from the alloy in four minutes as compared with four hours required to reduce the carbon 1.6 per cent. at a temperature just below the melting point of the alloy. The most promising condition for refining high-carbon ferro-chromium by this method is probably blowing the molten alloy with a blast of hydrogen in a converter.

RADIO-FREQUENCY AMPLIFIERS.[4]

By P. D. Lowell.

[ABSTRACT.]

ELECTRON tube amplifiers now form an essential part of all but the most simple radio receiving sets. By the use of a good amplifier a feeble signal may be made loud enough to be heard throughout a large room, and a signal which is so feeble as to be inaudible may be made loud enough to be clearly read. Amplifiers are in fact necessary to receive distant stations, or when using coil antennas. The received radio-frequency current may be amplified before it is rectified by a detector tube; this is called "radio-frequency amplification." Or the rectified output of the detector tube may be amplified; this is called "audio-frequency amplification." Persons desiring an elementary discussion of amplification may refer to the "Principles Underlying Radio Communication," Signal Corps Radio Communication Pamphlet No. 40.

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[4] *Scientific Papers*, No. 449.

An amplifier which has one tube used as a detector and two tubes used as amplifiers is said to have two *stages* of amplification. The simplest amplifiers have one or two stages of audio-frequency amplification. If it is desired to use four or more stages of amplification, it is necessary to use radio-frequency amplification as well as audio-frequency amplification. If the attempt is made to use more than three stages of audio-frequency amplification, serious disturbances are likely to be caused which will result in "howling" noises in the telephone receivers; these noises may be caused by regenerative effects. It is often advantageous to use radio-frequency amplification even if only one stage of audio-frequency amplification is used. A certain minimum signal is required for good operation of a detector tube, and if only a very feeble signal is being received, it is necessary that radio-frequency amplification be used in order that a signal of proper strength be delivered to the detector tube.

Radio-frequency amplification can make clearly audible a signal from a distant station which without such amplification is entirely inaudible. In a properly designed amplifier, the use of radio-frequency amplification often improves considerably the ratio of signals to strays. Radio-frequency amplification alone will not, however, give a signal strong enough to operate a loud-speaker, since the detector tube does not have sufficient output to operate a loud-speaker. If a loud signal is desired audio-frequency amplification should be used.

The small coil antennas used in direction finding work receive only a very feeble signal, and it is necessary to amplify these feeble signals many times if it is desired to do accurate direction finding work. This is particularly true if the minimum method of direction finding is used. Methods of direction finding are discussed in Bureau of Standards Scientific Paper No. 428, by F. A. Kolster and F. W. Dunmore, "The Radio Direction Finder and Its Application to Navigation."

A multistage amplifier consists of a number of electron tubes connected in suitable circuits. Each tube amplifies the signal impressed on its grid circuit and delivers the amplified signal from its plate circuit. The output or plate circuit of one tube is coupled to the input or grid circuit of the next tube by any one of several methods. It is important that efficient methods be used for transferring the signal energy from the plate circuit of one tube to the grid circuit of the next tube.

There are three methods by means of which the electron tubes may be coupled together so as to give amplification at radio frequencies; first, resistance coupling; second, tuned plate coupling; and third, transformer coupling.

With resistance coupling, it is customary to connect in the plate circuit of the first amplifier tube a non-inductive resistance of about 80,000 ohms, having as low a distributed capacity as possible, and to connect a condenser of about 0.0005 microfarad capacity from the plate of this tube to the grid of the next tube. The radio-frequency variations of the current in the plate circuit of the first tube cause corresponding variations in the voltage across the resistance and hence radio-frequency variations in the potential of the grid of the second tube. This method is, however, limited to amplification of relatively low radio frequencies, and will not usually give satisfactory results on frequencies much above 150 kilocycles per second with the tubes at present ordinarily available.

In the second method, tuned plate coupling, the plate circuit of the first tube is actually tuned to the signal frequency either by means of an inductance shunted by a variable condenser, or by a continuously variable inductor, inserted in series with the plate circuit.

The circuit is similar to the resistance-coupled circuit except that the coupling resistance is replaced by either a continuously variable inductor, or by an inductance shunted by a variable condenser. A condenser permits the radio-frequency currents to flow from this plate to the grid of the next tube as in the resistance-coupled method. The tuned plate method is more efficient than resistance coupling at frequencies above 150 kilocycles per second.

The third method, transformer coupling, is the most efficient and therefore most desirable, and it is this method for which circuits were developed and which is discussed in this paper.

In all the circuits of a radio-frequency amplifier it is necessary to keep all capacities as low as possible. It is therefore necessary to use transformers whose windings have small distributed capacity, and to use electron tubes having small capacities between the elements.

It has been found that either air-core or iron-core transformers may be used for coupling the output circuit of one tube to the input circuit of the next. The air-core type gives more amplification per stage, but on the other hand, is responsive to only a narrow band of frequencies owing to the low effective resistance of its windings.

The iron-core type, while not giving as much amplification per stage, will allow amplification over a much broader band of frequencies.

However, a special form of air-core transformer has been developed for radio compass work, which will respond to signals on wave-lengths from 600 to 1000 metres by means of a simple and quick adjustment.

The coils of this air-core transformer were wound with No. 38 B. & S. gauge single-silk-covered copper wire in the form of a pancake or flat doughnut, as it is sometimes called, and are impregnated with insulating varnish to make them self-supporting. The wire was wound in a manner similar to the so-called " honeycomb " coils, or, as the British call it, a " basket " winding.

Two of the coils coupled together constitute an air-core radio-frequency transformer, one coil being connected in the plate circuit of one tube and another connected in the grid circuit of the succeeding tube, in the usual manner.

Several six-stage amplifiers have been made, utilizing iron-core radio-frequency coupling transformers, and have given very good results.

In constructing an iron-core transformer, the primary and secondary windings are wound on a square insulating tube in two single layers, side by side. A core made up of silicon steel laminations about the thickness of a piece of tissue paper is placed inside the insulating tube.

The construction of a radio-frequency amplifier is quite a difficult task and requires no little amount of patience and resourcefulness, but when constructed properly is, of course, extremely useful for the reception of signals with a coil aerial. The coil aerial permits the elimination of undesired and interfering signals by rotation of the coil to the point where the unwanted signals drop out.

AN ELECTRON TUBE AMPLIFIER USNG 60-CYCLE ALTERNATING CURRENT TO SUPPLY POWER FOR THE FILAMENTS AND PLATES.[5]

By P. D. Lowell.

[ABSTRACT.]

ELECTRON tube amplifiers form an important part of practically all radio receiving sets now, except the most simple types. Such amplifiers are in fact necessary to receive distant stations, or when using coil antennas. For good operation, amplifier tubes require for the filament a source of voltage of very constant value (usually about 6 volts) and for the plate a source of voltage of from 40 to perhaps 300 volts. The filament voltage is usually supplied by storage cells, and the plate voltage by dry cells. The maintenance of these cells in operating condition, especially the storage cells, is often a source of much difficulty and annoyance. The storage cells are necessarily bulky and heavy, require constant attention to maintain proper charge and density of electrolyte, and give off injurious acid or other fumes. The development of an amplifier which can be supplied from the ordinary 110-volt a.c. lighting mains is of considerable practical importance, since it would eliminate the practical difficulties of maintaining storage cells. The amplifier using such a.c. supply has the important advantages of reliability, convenience, and cheapness both in first cost and operating cost.

Such an amplifier using five stages of amplification has been developed at the Bureau of Standards. There are three stages of radio-frequency amplification and two stages of audio-frequency amplification. This paper describes this amplifier briefly.

The voltage for the filaments is obtained from one winding of a 60-cycle transformer having four windings. The primary is connected to the 110-volt 60-cycle a.c. lighting supply. The grid circuits, instead of being connected directly to one terminal of the filament supply, are connected to an intermediate point between the filament supply terminals through the medium of a slide-wire voltage divider, the ends of the voltage divider being across the filament supply and the grid circuits being connected to the sliding contact through a one microfarad condenser shunted by a one megohm leak resistance. One voltage divider is used for the grids of the radio-frequency tubes and one for the grids of the audio-frequency tubes. By adjusting the sliders of the voltage divider, the grids may be brought to a value of voltage which is constant with respect to the changing voltage of the filament, thereby reducing the a.c. hum. The one microfarad series condensers serve to allow the grids to assume a favorable condition for amplifying. It was found to be more desirable to replace the condenser and leak resistance in the grid leaks of the audio-frequency tubes with a 10-volt negative dry battery which gave better amplification with less hum.

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[5] *Scientific Papers*, No. 450.

It was found that a crystal detector gave much better operation with less hum than a tube detector because the former can be entirely insulated from the a.c. power circuit and picks up less hum than the tube detector.

Plate voltage is supplied from another winding of the 60-cycle transformer, the a.c. voltage being rectified by means of a two-electrode electron tube and smoothed out by large condensers to make it suitable for use on the plates of the amplifier tubes. The paper gives diagrams of various circuits used in the course of development and the final circuit employing five amplifier tubes.

This final circuit gives good amplification, with a slight residual hum which is not great enough to be objectionable when receiving signals of ordinary readable strength. The residual hum is of course more objectionable when extremely weak signals are being received. Radio telephone music and conversation are clearly reproduced.

The amplifier was operated under normal conditions using the usual sources of direct-current supply, and then switched over to alternating-current supply. This comparative test showed the a.c. supply to give as good amplification as the d.c. supply, although the set was slightly more sensitive to weak signals when batteries were used, on account of the interference caused by the hum when used on a.c. supply.

For the reception of damped waves, the amplifier as constructed operated most satisfactorily for frequencies from 400 kilocycles to 1500 kilocycles per second (750 to 200 metres). This frequency range was determined by the working range of the radio-frequency transformers used. By using suitable radio-frequency transformers, it is expected that the amplifier will be effective for the reception of damped waves for frequencies as low as 30 kilocycles (10,000 metres). This amplifier has also been found effective for the reception of undamped waves, when used with a separate heterodyne.

The use of a loud-speaking telephone receiver such as the "Magnavox" was made possible by applying to the field coil of the loud-speaker an alternating current rectified by a "Tungar" rectifier tube. The impedence of the field coil was sufficient to smooth out the pulsating current to such an extent that the hum was not annoying. It was also advantageous to couple the loud-speaking reproducer circuit to the plate circuit of the last amplifier tube by means of a one-to-one ratio telephone transformer with a 0.02 microfarad condenser in series with the telephone circuit.

SPECTROPHOTOELECTRICAL SENSITIVITY OF BOURNONITE AND PYRARGYRITE.[6]

By W. W. Coblentz and J. F. Eckford.

[ABSTRACT.]

THE present paper, considered in connection with previously published data on proustite (Bureau of Standards Scientific Papers, No. 412), represents a study of the effect of chemical constitution upon spectrophotoelectrical sensitivity.

Experimental data are given on the effect of temperature and of the intensity of the radiation stimulus upon the photoelectrical sensitivity of the minerals bournonite and pyrargyrite, in the spectral region extending from 0.3μ in the ultra-violet to 2μ in the infra-red.

The spectrophotoelectrical reaction curve of bournonite is entirely different from that of the constituent sulphides of copper and lead (which are not photo-sensitive) and of antimony which has its photoelectrical sensitivity confined principally to a band at 0.77μ in the extreme red. On the other hand, bournonite has a high spectrophotoelectrical sensitivity extending from the extreme violet to 1μ in the infra-red, with two wide, ill-defined maxima in the region of 0.55μ and 0.95μ respectively.

On lowering the temperature the intrinsic spectrophotoelectrical sensitivity of bournonite is greatly increased and the maxima shift towards the short wave-lengths. The maximum in the violet usually remains the more intense at the lowest temperatures.

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[6] *Scientific Papers*, No. 451.

The spectrophotoelectrical reaction of the mineral pyrargyrite, which is a double sulphide of silver and antimony, is entirely different from that of the constituent sulphides of silver and of antimony, which also exhibit photosensitivity.

At 22° C. the photoelectrical reaction of pyrargyrite consists of a wide unsymmetrical maximum in the ultra-violet, with a weak, ill-defined maximum in the region of 0.63μ.

At low temperatures, $-165°$ C., pyrargyrite reacts electrically to radiations of all wave-lengths extending from the extreme ultra-violet to 1.5μ in the infra-red; but the greatest photoelectrical reaction is localized in the band at 0.63μ.

There is a great similarity in the spectrophotoelectrical and chemical properties of pyrargyrite (silver-antimony sulphide) and of proustite (silver-arsenic sulphide). In a general way, the foregoing properties of photoelectrical reaction spectra are analagous to properties of absorption spectra, as affected by chemical constitution, from which it appears that perhaps ultimately the two phenomena may be traced to a common source within the molecule.

THE PREPARATION OF IRON-CARBON-MANGANESE ALLOYS AND THE EFFECTS OF CARBON AND MANGANESE ON THE MECHANICAL PROPERTIES OF IRON.[1]

By R. P. Neville and J. R. Cain.

[ABSTRACT.]

THIS paper describes the preparation and mechanical properties of a series of very pure alloys of electrolytic iron, carbon, and manganese, whose compositions were so chosen as to bring out the specific effects on pure iron of: (1) additions of carbon; (2) additions of manganese; and, (3) additions of carbon and manganese together in varying relative proportions. The maximum amount each of carbon and manganese in each series was about 1.5 per cent.; the minimum, 0 per cent., or pure iron.

The alloys were made in three-pound ingots by melting electrolytic iron in an electric vacuum furnace, in a crucible of pure magnesia, to which the carbon and manganese were added after fusion of the iron. From these ingots tensile test specimens were made and tested in the annealed condition.

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[1] *Scientific Papers,* No. 453.

Data are tabulated and grouped so as to bring out the effects of each element. From these data curves were constructed which show graphically the effects of carbon and of manganese on the mechanical properties of the alloys.

Carbon increased the ultimate strength of the iron at an average rate of about 1000 lbs. per sq. in. for each 0.01 per cent. carbon, up to a content of about 0.85 to 1.0 per cent., the rate increasing with the increase in manganese. The proportionate increase in Brinell hardness was about the same as that for ultimate strength. The proportional limits were less affected by carbon than were the ultimate strengths. Elongation and reduction of area were rapidly reduced as the carbon increased.

Manganese, in the absence of carbon, had very little effect on the mechanical properties of iron. With the addition of carbon its effect was increased proportionately with the carbon content, raising the ultimate strength from 90 to 250 lbs. per sq. in. for each 0.01 per cent. manganese. Brinell hardness was increased in about the same manner. The proportional limit was increased more by manganese than was the ultimate strength. The effect of manganese on ductility was negligible.

Further Studies on the Electron Theory of Solids. Sir J. J. Thomson. (*Phil. Mag.*, October, 1922).—The arrangement of atoms and electrons is pretty well known for calcium. From consideration of the electrical forces involved Sir J. J. Thomson computes its compressibility to be 5.9×10^{-12}, which agrees with Richards' measured value of 5.5×10^{-12}. In the case of the diamond the calculated value of the compressibility agrees quite closely with that of Adams but is only one-third of that found by Richards.

The old method of using the electrons to explain the transfer of heat and of electricity was to consider them as moving about rather freely within the conductor. Now their motion is regarded as far less free. In a metal all the electrons occupy definite positions in relation to the atoms and a whole series of them lie in a row. By the motion of such a row of electrons the author proceeds to show how both heat and electricity are transferred and he succeeds so well that he arrives at a formula that embodies the Wiedemann-Franz law according to which "the ratio of the thermal to the electrical conductivity should at the same temperature be the same for all metals, and at different temperatures should be proportional to the absolute temperature." And this is not all, for he furnishes an explanation of the super-conductivity of lead at low temperatures, discovered by Kammerlingh Onnes.

G. F. S.

NOTES FROM THE RESEARCH LABORATORY EASTMAN KODAK COMPANY.*

NOTE ON THE RELATION BETWEEN SENSITIVENESS AND SIZE OF GRAIN IN PHOTOGRAPHIC EMULSIONS.[1]

By S. E. Sheppard and A. P. H. Trivelli.

In confirmation of Mr. Renwick's emulsion experiments an experiment reported shows that coarse-grained emulsions are not always more sensitive than fine-grained ones, although in the same emulsion statistically there is a probability of greater sensitivity for larger grains. From a theoretical treatment of the subject the conclusion is drawn that the catalytic effect of silver nuclei depends on orientation in relation to the silver halide crystal lattice, and that in turn on the exposure. It is noted that the difference in effect on clumps of grains of developers of high and low reduction potentials should be considered in the experimental work.

QUANTUM THEORY OF PHOTOGRAPHIC EXPOSURE.[2]

By L. Silberstein.

After a short introduction concerning the structure of the photographic plate, the assumption is made that light consists, either entirely or in part, of discrete energy parcels or light darts, each containing a quantum of energy, and that a silver halide grain is affected, *i.e.,* made developable whenever it is hit by one or more light darts of a sufficiently high frequency or of a sufficiently short wave-length. With these assumptions the problem of the production of the latent image is reduced to a problem in probabilities and its solution gives the percentage number of grains affected as an exponential function of the size (area) of the particular class of grains and of the number of light quanta thrown upon the plate. The integral effect ranging over any finite interval of sizes is then deduced. Further the dependence of the number of affected grains upon wave-length is discussed in connection with a possible finite cross-section of the light darts. Finally the aforesaid exponential formula, supplemented by a term corresponding to a finite section of the light missiles, is tested on a series of thirty-three microphotographic observations on grain clumps made for this purpose by Trivelli and Righter. Each clump of the special experimental emulsion being considered as a single photographic unit or target, of area equal to the sum of the areas of its component grains, the theoretical percentage numbers of clumps affected by a unique exposure are found to agree very accurately with the observed ones over a range of sizes from 0.75 – 25.0 square microns, the corresponding percentage numbers of units affected ranging for the thirty-three classes, from 16 to full 100 per cent. These results are tabulated numerically and represented by a graph. The tests afforded by other experiments and some further theoretical deductions will be published shortly in the same journal.

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* Communicated by the Director.

[1] Communication No. 128 from the Research Laboratory of the Eastman Kodak Company and published in *Phot. J.,* November, 1921, p. 400.

[2] Communication No. 139 from the Research Laboratory of the Eastman Kodak Company and published in *Phil. Mag.,* July, 1922, p. 257.

ON THE MUTUAL INFECTION OF CONTIGUOUS SILVER HALIDE GRAINS IN PHOTOGRAPHIC EMULSIONS.[3]

By A. P. H. Trivelli, F. L. Righter, and S. E. Sheppard.

THIS paper gives a brief discussion of the results obtained by T. Svedberg when using a special emulsion furnished by F. F. Renwick and a ferrous oxalate developer. It is pointed out that the results of Svedberg directly contradict results obtained by Svedberg's method in this laboratory. A description of the work with photomicrographs, curves and resultant data is given. The wide deviation in results obtained in the two curves is thought to be due largely to the great difference in the type of emulsion used.

Ratio of Mass to Weight for Bismuth and Aluminium. H. A. WILSON. (*Phys. Rev.*, July, 1922).—Brush has described experiments which seem to show that the ratios between mass and weight are different for different substances, and that this is especially the case with bismuth and aluminium. Now from the Rice Institute comes a fresh determination for the same two substances by the method of Eötvös. The conclusion is that the acceleration is the same for both elements to within one part in a million. G. F. S.

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[3] Communication No. 146 from the Research Laboratory of the Eastman Kodak Company and published in *Photo. J.*, September, 1922, p. 407.

NOTES FROM THE U. S. BUREAU OF CHEMISTRY.*

PROGRESS IN THE PHYSICAL CHEMISTRY OF GELATIN.[1]

By C. R. Smith.

[ABSTRACT.]

CHEMICALLY pure gelatin cannot be said to have been prepared as yet. Recent studies of the physico-chemical properties of gelatin, including the mutarotation, osmotic pressure, and swelling, define the quality of material used. "Ash-free" gelatin, with interesting properties, has been prepared and used in experimental work where small and unmeasured amounts of electrolyte impurities nullify the results.

The osmotic pressure and swelling of gelatin sols and gels in acids and alkalies has been shown to be ionic phenomena dependent on the extent of combination, ionization, valency, and quantity of ions opposite in charge to the gelatin present. Recent work has been considered as proving the distribution of acids, bases, and salts between gelatin and water separated by a semipermeable membrane to follow Donnan's theory of membrane equilibrium. The writer, however, points out certain fundamental requirements of this theory which have not yet been verified.

THE INFLUENCE OF ATMOSPHERIC HUMIDITY ON THE STRENGTH AND STRETCH OF LEATHER.[2]

By F. P. Veitch, R. W. Frey and L. R. Leinbach.

[ABSTRACT.]

THE effect of humidity on the physical properties of certain fibrous materials such as paper has been recognized for some time, as is shown by the testing of this material under controlled conditions of temperature and relative humidity. It begins to appear that such practice will be necessary in testing leather, especially for research studies. For an ungreased, vegetable-tanned leather a surprisingly great effect from humidity is shown, and it is

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* Communicated by the Chief of the Bureau.

[1] Published in *J. Am. Leather Chemists' Assoc.*, 17, Oct., 1922, 508.

[2] Published in *J. Am. Leather Chemists' Assoc.*, 17, Oct., 1922, 492.

probable that on most, if not all, leathers there is an influence too great to be safely ignored.

For a comparison of two different relative humidities a section of leather from the prime location in the side was cut into 180 test pieces. Alternate pieces were tested at one condition and the remainder at the other. Charts, prepared to show the data for the individual test, show incidentally the marked lack of uniformity in the physical properties of a given piece of leather. The test pieces were conditioned, weighed, and tested within a special constant temperature—constant humidity room, automatically controlled twenty-four hours of the day. The temperature was kept at 70° F. throughout the experiments.

The following grand average results were obtained: For an increase of 20 per cent. relative humidity, from 35 to 55 per cent., the increase in tensile strength was 12.9 per cent. and in elongation 15.7 per cent. For an increase of 40 per cent. relative humidity, from 35 to 75 per cent., the gain in tensile strength was 42.3 per cent. and in elongation 53.1 per cent. The increases, while not directly proportioned to the increase in relative humidity, are very closely parallel to the percentage gain in moisture.

A COMPARATIVE STUDY OF SPOILAGE IN SALMON.[3]

By Albert C. Hunter.

[ABSTRACT.]

IN a study of the spoilage of mature humpback salmon caught on the spawning migration in Puget Sound and of humpback salmon taken from the spawning grounds of the Green River, it was found that a somewhat different rate and a different type of spoilage take place in the two groups of fish. The difference in the total number of bacteria in the gills, in the flesh of the back and belly, in the pyloric coca, in the stomach, and in the intestines of the two groups of salmon was not great enough to explain the difference in the rate of spoilage. A study of the aerobic and anaerobic organisms representing the bacterial flora of these decomposing salmon indicates that practically the same bacteria are responsible for the decomposition of both groups of salmon.

In addition to the bacteria which have been previously described by the author as being responsible for the decomposition

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[3] Published in *Am. Food J.*, 17, Sept., 1922, 19.

of salmon, several sporulating anaerobes were isolated from the decomposing fish.

It is probable that the difference in the rate and type of spoilage in the two groups of salmon is due to a marked difference in chemical composition of the fish, rather than to any appreciable difference in bacterial flora.

SOME EXPERIMENTS WITH A BORIC-ACID CANNING POWDER.[4]

By Ruth B. Edmondson, Charles Thom and L. T. Giltner.

[ABSTRACT.]

A BORIC-ACID canning powder was examined in the Bureau of Chemistry. In the quantity recommended it exerted a selective antiseptic action toward certain molds and members of the aerobic group of microörganisms in test-tube experiments. These groups are not responsible for spoilage in properly processed cans or jars, and may therefore be disregarded for the present purposes. The powder in the quantity recommended for canning had no inhibitory effect on representative members of the anaerobic spore-forming group, especially the toxin-forming *B. botulinus,* which has recently been responsible for many deaths from food poisoning.

In the practical canning experiments the use of the powder for acid products was shown to be an unnecessary and wasteful practice, since material packed without the powder kept as well as that packed with it. Its use with the more or less neutral vegetables showed that the powder plus the inadequate heating recommended was not sufficient to preserve the materials or to prevent the production of toxin in them by *B. botulinus.*

Influence of Changes in the Radiation and Activity of the Sun Upon Conditions on the Earth. G. ANGENHEISTER. (*Verh. Deutschen Physik. Gesell.,* Dec. 31, 1921.)—When the number of sun spots is at its maximum, the sun itself is hotter than usual but the earth, strange to say, is cooler.

The evidence for a higher temperature on the sun at that time is:

(*a*) Abbot's determination that the solar constant is then a maximum. There is a difference of 2½ per cent. between its maximum and its minimum values.

(*b*) In general the distribution of brightness over the disc of the sun corresponds to what would be expected in the case of equilibrium in radiation. At sun spot maximum, however, there is a greater contrast between the appearance of the circumference and the middle of the disc, and the appearance approaches that which would accompany adiabatic equilibrium in the atmosphere of the sun. There are, then, stronger vertical movements. The cooler outer layers sink and are replaced by hotter masses. Thus the sun looks hotter and really radiates more energy.

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[4] Issued as U. S. Dept. Agr. Cir. 237, Aug., 1922.

(*c*) The brightness of Jupiter and of Enke's comet varies in an eleven-year period and is greatest at sun spot maximum.

Similarly the mean temperature of the earth follows the eleven-year sun spot period, but it is at its minimum just when the number of spots is greatest. Thus when the sun radiates most the earth is coolest. True the difference is not great, as the amplitude of the eleven-year temperature is only .5° C. at continental stations. The observations at Samoa, extending over thirty years, show the same thing precisely, though with a little larger amplitude.

Why is the earth cooler when the sun has its highest temperature? The wind records at Samoa likewise exhibit an eleven-year periodicity. At the time of sun spot maximum the trade winds are 10 per cent. more frequent than at the time of minimum. The influx of cooler air from higher latitudes is greater at the sun spot maximum, and the temperature of Samoa is lowered. Moreover the frequency of cirrus clouds in like manner displays the familiar eleven-year course, which has its maximum at the time of sun spot maximum. Thus at that time the albedo of the earth grows larger and more energy is sent back into space. The atmosphere absorbs .05 calorie per square cm. less in a minute, and the mean temperature of the earth drops a fraction of a degree. G. F. S.

Anemometer Investigations. (*U. S. Department of Agriculture Clip Sheet No. 225.*)—Through studies conducted by the Weather Bureau with the coöperation of the Bureau of Standards, much information useful in the design and construction of anemometer instruments for measuring wind velocities has been obtained. The relation between cup movement and actual wind movement, heretofore known confidently to about 50 miles an hour, is now known to 113 miles an hour.

Tests on about 30 instruments of various dimensions, proportions, and weights have been made in the wind-tunnels of the Bureau of Standards at velocities ranging from 5 to 60 metres per second. Certain of the instruments tested in the wind-tunnels have been taken to Mount Washington, N. H., for comparison in the very high natural winds prevailing there. When these free-air comparisons are completed and the data have been analyzed, an improved standard anemometer recording true velocities will be developed and corrections determined for records of velocity already compiled.

NOTES FROM THE U. S. BUREAU OF MINES.*

FUSIBILITY OF ASH FROM COALS OF THE UNITED STATES.

By W. A. Selvig and A. C. Fieldner.

The Bureau of Mines has made a general survey of the "fusing" or "softening" temperatures of the ash from coals in the United States. Data on the fusibility of coal ash should be of considerable value to the coal consumer, mainly in connection with the troublesome formation of clinker resulting from the melting of the ash constituents in burning coal. When used together with the large number of coal analyses published by the bureau, it will assist the consumer in comparing different coals and in selecting the coal best adapted to his purpose.

The ash is the incombustible residue after complete combustion, and is derived from the inorganic mineral constituents. These are (1) inherent impurities in intimate mixture with the coal substance, (2) impurities such as clay, shale, pyrite, and calcite that are present as partings, layers, or nodules in the coal bed, and (3) fragments of roof or floor mixed with the coal in mining.

Coal ash varies so widely in chemical composition that no typical composition can be given, but generally falls within the following limits: Silica, 40 to 60 per cent.; alumina, 20 to 35 per cent.; iron oxides, 5 to 25 per cent.; lime, 1 to 15 per cent.; magnesia, 0.5 to 4 per cent., and alkalies, 1 to 4 per cent. The fusibility depends on several factors, such as ratio of bases to silica present, the particular bases, and the percentage of alumina. For example, ash extremely high in silica or in bases is not readily fusible. Ash low in iron is usually so high in silica that it is not readily fusible. Ash of coals high in pyrite contains much iron, and is likely to form clinker, the iron converting to ferrous oxide which unites with silica to form easily fusible silicates.

Some coal ash is so infusible that little clinker is formed, and ash slightly fusible often forms a porous, spongy clinker that does not obstruct flow of air through the fuel bed and is easily removed. Ash with a low fusing temperature, say 2100° F., may become quite fluid and spread out in a thin sheet, obstructing flow of air and localizing the heat in the fuel bed.

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* Communicated by the Director.

In general, the softening temperature of ash from coals in the United States ranges from 1900° to 3100° F., and may be classed as (1) refractory ashes, softening about 2600° F.; (2) ashes of medium fusibility, softening between 2200° and 2600° F., and (3) easily fusible ashes, softening below 2200° F.

Further details will be found in Bulletin 200 recently issued by the bureau.

ARC REGULATION IN ELECTRIC FURNACES AND PILOT LIGHT CONTROL.

By C. E. Sims.

In any furnace where two or more electrodes are used, one of the main problems in operation is the proper regulation of the electrodes. There are available a number of automatic control systems which, when functioning properly, give excellent regulation and an even, well-balanced load. These are expensive, however, and for small furnaces are often impractical, so that a large proportion of the furnaces are hand-operated.

An apparatus devised in the bureau's laboratory and used on an experimental single-phase furnace furnishes an accurate and sensitive control, and can be home made at low cost.

Two 40-watt tungsten bulbs are set upright on a shelf near the meter board and in full view from the hand controls. Each lamp is connected to one electrode (or bus bar); both lamps have a common connection to the metal bath in the furnace. Usually all that is necessary is to connect them to the shell of the furnace, but if that does not work, a steel bar can be buried in the hearth. In operation the brilliancy of the filament will vary with the drop in potential between the electrode and the bath. A lamp of this type will glow dull red at 15 volts and will safely stand surges up to 125 volts. When the power is on and no arc has been drawn the lamps will simply be in series across the bus bars and will glow with equal brilliancy. When current is flowing through the furnace they are lighted equally only when both arcs are exactly the same, that is, have the same length and, therefore, the same resistance. The slightest change in either arc is quickly and accurately indicated by the lamps. If one electrode should touch the bath its pilot light would instantly go black. These lights, therefore, show the exact position of the electrodes at all times. For three-phase operation it is necessary merely to add one more lamp.

A more detailed account is presented in a report issued by the bureau in mimeograph form.

THAWING FROZEN GRAVEL IN PLACER MINING.

By Charles Janin.

The working of frozen gravels, a special problem in placer mining, has received much attention in Alaska and the Yukon Territory. The expense of thawing with steam points, the chief method of thawing frozen gravel for drift, surface mining, or dredging operations, has prevented the working of the lower-grade gravels in the frozen areas. About 1915, different persons started experimenting with an entirely new plan for softening the gravel. Water at natural summer temperature was applied by means of holes drilled through the frozen muck and gravel to bedrock, with satisfactory results. The method was taken up in the Dawson field by the Yukon Gold Company and the Canadian Klondike Company; at Nome, by the Alaska Mines Corporation, on Candle Creek by Edward Pearce, and others. While there is much to be learned regarding its practical application, it has passed the experimental stage and is proving of great value to the gold-mining industry.

Its successful application where water is obtainable under pressure without pumping will make large areas of low-grade ground available for dredging, and ground that previously has been considered of little value now will be of economic importance.

Details are presented in Technical Paper 309, "Recent Progress in the Thawing of Frozen Gravel in Placer Mining," published by the Bureau of Mines.

The Effect of Nascent Hydrogen on Hardening Steel Magnets. John Coulson. (*Phys. Rev.*, July, 1922).—Fifty or more steel bar magnets, 14.4 cm. long, were quenched to glass hardness at 850° or were hardened at 700°. They were then magnetized to saturation inside of a solenoid. After this they were alternately heated and cooled until no further change in the magnetic moment was observable. Finally each magnet was made the cathode in an electrolytic cell containing a solution of sulphuric acid. The current, kept at two amperes, caused the evolution of nascent hydrogen upon the surface of the magnet. This was followed by a loss of magnetic moment. In the case of drill rod steel after an hour the moment had fallen by about 4 per cent., the liquid being at 20° C. "From two to three hours' exposure to the electrolytic hydrogen decreased the magnetic moment of the magnet to a fixed value. Hammering the magnets had little or no effect in changing further their magnetic moment. Careful weighing before and after treatment showed that the magnets did not lose weight during exposure. . . . The rapidity with which the magnetic moment settles to a final value depends on the temperature of the electrolyte in which the magnets are brought under the action of the electrolytically evolved hydrogen. Moreover, the transition to the final state, due to the action of the hydrogen, is surprisingly different for the different specimens."

Special magnet steel, a tungsten alloy steel, after having been exposed for some time to the hydrogen, showed a sudden fall in the value of its moment. This was especially marked when the quenching occurred at 700°. One specimen lost in three minutes as much as 11 per cent. of its moment. The continuance of the treatment for eighteen minutes made scarcely any further difference.

When the magnets were broken the fracture showed that the hydrogen had penetrated within the steel. It is known that the magnetic permeability and also the specific resistance are modified by the process. G. F. S.

Research on Liquid Carbon Dioxide.—The Liquid Carbonic Division of the Compressed Gas Manufacturers' Association announces the establishment of an Industrial Fellowship in the Mellon Institute of Industrial Research of the University of Pittsburgh, for the purpose of classifying, studying and developing the uses for liquid carbon dioxide. The founding of this Fellowship is in accord with the desire of the members of the Association to coöperate with users and prospective users of liquid carbon dioxide, with the object of developing efficient means of applying the gas and of obtaining fundamental data bearing on its use in various industries.

In addition to conducting research work, the Fellowship will be made a clearing-house of information regarding various uses of liquid carbon dioxide, and data will be kept on file for the accommodation of prospective users of this product.

The present incumbent of the Industrial Fellowship is Charles L. Jones, who will be glad to correspond with anyone interested in the use of liquid carbon dioxide in industry.

THE FRANKLIN INSTITUTE.

(*Proceedings of the Stated Meeting held Wednesday, November 15, 1922.*)

HALL OF THE FRANKLIN INSTITUTE,
PHILADELPHIA, November 15, 1922.

MR. W. C. L. EGLIN, Vice-president, *in the Chair.*

The Board of Managers submitted its report. The report recorded the election to membership of:

Robert Atkinson, Esq., Teacher, Haverford College, Haverford, Pennsylvania.

Gustav Egloff, Esq., Ph.D., Chemist, 208 South La Salle Street, Chicago, Illinois.

Walter M. Mitchell, Esq., Ph.D., Metallurgical Engineer, 112 North 34th Street, Philadelphia, Pennsylvania.

Harry K. Rutherford, Esq., Major, Ordnance Department, U. S. A., Frankford Arsenal, Philadelphia, Pennsylvania;

lectures before the Sections as follows:

"High-speed Photography of Vibrations" by
Augustus Trowbridge, Ph.D.,
Professor of Physics,
Princeton University,
Princeton, New Jersey,

"The Spectrum of Neutral Helium and the Behavior of Its Two Electrons" by
Ludwik Silberstein, Ph.D.,
Research Laboratory,
Eastman Kodak Company,
Rochester, New York,

"Structural Colors in Feathers" by
Wilder D. Bancroft, Ph.D.,
World War Memorial Professor of Physical Chemistry,
Cornell University,
Ithaca, New York,

and a lecture before the Stated Meeting October 18, 1922, by
Arthur L. Day, Ph.D., Director,
Geophysical Laboratory,
Carnegie Institution,
Washington, D. C.
on "The Study of Earth Movements in California;"

also additions to the library by gift, 23 volumes and 70 pamphlets, by purchase, 17 volumes and by binding, 128 volumes.

The Chairman then announced that final action would be taken on the following resolution to amend the By-Laws as recommended by the Board of Managers to the Institute at its Stated Meeting of October 18th last:

> "RESOLVED, That the words 'in the way and manner hereinafter provided so that the same shall not in any event be liable for the debts of the Institute,' in Section 1 of Article 1 be omitted and stricken therefrom, and that the last paragraph of Section 6 of Article 1, as follows: 'The principal and interest of all trust funds shall not be liable for debts of the Institute but shall be devoted to its continuance and preservation,' be omitted and stricken therefrom, and that Section 1 of Article 1 and Section 6 of Article 1 be amended so as to read as now expressed with the omission of the said words."

On motion, duly seconded, the resolution was unanimously adopted.

Doctor Hoadley offered the following resolution which was seconded by Doctor Cope and passed unanimously:

> "RESOLVED, That a committee of three be appointed to nominate officers and managers for the year 1923."

The Chairman then announced that the next business of the meeting would be the presentation of awards made by the Institute on recommendation of its Committee on Science and the Arts and recognized Dr. Thomas D. Cope.

Doctor Cope said, "Mr. Chairman, Members of the Institute, Ladies and Gentlemen: It is the custom of the Committee on Science and the Arts each year to review all the articles that have appeared in the JOURNAL OF THE INSTITUTE during the year, with a view to selecting for recognition those articles which appeal to the Committee as possessing especial merit.

"The highest award which the Committee is empowered to make for an article of superior excellence in the JOURNAL is the Howard N. Potts Gold Medal.

"For the year 1921, the Committee has selected the paper on 'Helium, Its History, Properties and Commercial Development,' by Dr. Richard B. Moore, Chief Chemist, United States Bureau of Mines. This paper appeared in the JOURNAL OF THE INSTITUTE for February, 1921.

"In this paper the romantic story of helium is completely and authentically told. In selecting this paper for the highest recognition, the Committee has not been unmindful of the fact that the author has witnessed the development of the story which he tells and has taken a foremost part in the making of that story.

"I have the honour, Mr. President, to present to you, Dr. Richard B. Moore, Chief Chemist of the United States Bureau of Mines, to receive from you the Howard N. Potts Medal for his paper on 'Helium, Its History, Properties and Commercial Development.'"

The Chairman then presented the Medal and Accompanying Certificate to Doctor Moore, who in acknowledging this recognition, said,

"Mr. President, Members of the Institute, Ladies and Gentlemen: I desire to thank you, the Chairman, and the Members of The Franklin Institute, most heartily for the honour conferred upon me. I naturally feel somewhat overwhelmed that this honour should have come from The Franklin Institute, and

I appreciate it all the more strongly because of my personal interest in the Institute, which has extended over a number of years.

" For your information I may say that at the present time about 15,000 cubic feet of helium is being extracted each day, and stored in tanks, and within a couple of months, I hope that this figure will be raised to between 30,000 and 40,000 cubic feet per day. As there were only about 10 cubic feet of helium in the world before the war, this represents some real progress even though we have a considerable way still to go."

The Chairman then recognized Dr. George A. Hoadley who introduced Dr. C. W. Colby, President, The Noiseless Typewriter Company, New York City.

Doctor Hoadley said, " Mr. President: It would be most interesting to know how man first began to formulate a spoken language by means of which he could communicate his ideas to his neighbor.

" Even more interesting would be accurate information as to how this primitive man first began to communicate these ideas to his neighbor when he was no longer present to hear the spoken word. That this was done we know, for crude carvings and clay tablets and stone records have come down to us.

" From these beginnings has developed the art of manually written language by the use of the pen and pencil. With the advancement of civilization and the increase of business correspondence came the demand for a more rapid method of communication than either the pen or the printing press could supply. This demand was met by the invention of the typewriter, many kinds of which are in use.

" One objectionable feature, common to these machines is the insistant and distracting noise of the hammer blow of the type against the platen in the process of typing, a blow for every letter.

" This feature called for removal and a typewriter has been devised, developed and placed within our reach that makes it possible to operate one or more of these Noiseless Typewriters in a room and still be enabled to carry on the other business of an office without interference. This is done by substituting for the hammer blow stroke a pressure stroke.

" ' In consideration of the ingenuity shown by the inventors, the excellence of design and construction as exhibited in the machine, resulting in a thoroughly successful commercial noiseless typewriter, The Franklin Institute awards its Edward Longstreth Medal to The Noiseless Typewriter Company of New York.'

" Mr. President, I take pleasure in presenting Dr. Charles W. Colby, President of The Noiseless Typewriter Company, of New York."

The Chairman then presented the Medal, Certificate and Report to Doctor Colby who in acknowledging this recognition said:

" Mr. President, Members of the Institute, Ladies and Gentlemen: It was the saying of the Romans that there was no greater satisfaction in life than to be praised by one who is himself highly honoured; and it is because The Franklin Institute has been for so many years held in such high honour that The Noiseless Typewriter Company is profoundedly indebted to it for this high award.

" We are living in an age when the principle of authority is not perhaps so strong as at some periods in the past—perhaps not strong enough. But fortunately The Franklin Institute is a source of authority and the credentials received from it confer international honour.

"This is not the place for a harangue about The Noiseless Typewriter, regarding which Doctor Hoadley has spoken so appreciatively. However, one may point out that the writing machine is an indispensable part of modern civilized life. It used to be said that the pen is mightier than the sword and, changing the terms somewhat, it may now be said that the typewriter is mightier than the machine-gun, but that is no reason why it should make as much noise as a machine-gun.

"The Noiseless Typewriter is not a vegetable product that grows in the woods, and it took twenty years of hard work to develop it. I am very happy to say that some of the engineers who have contributed most to its development—including Mr. Kidder, Mr. Ruffin and Mr. Going—have lived to see the result of their labours and are here this evening.

"As regards The Noiseless Typewriter Company, I may say that those who constitute its membership have not been actuated merely by a desire for commercial gain, but have felt that they were engaging in a useful, constructive work. No recognition received by our Company is as much appreciated as this honour bestowed by The Franklin Institute."

The paper of the evening on "Animal Luminescence" was then presented by E. Newton Harvey, Ph.D., Professor of Physiology, Princeton University, Princeton, New Jersey. A review of the general facts of animal luminescence was first given. The physical nature of animal light, its relation to inorganic luminescences, and the chemical processes underlying its production were also considered. Special attention was given to the factors determining the intensity of luminescence and the possibility of obtaining a continuous luminescence was discussed. The subject was illustrated by lantern slides and demonstrations.

After a brief discussion the unanimous thanks of the meeting were extended to the speaker.

Adjourned.

R. B. Owens,
Secretary.

COMMITTEE ON SCIENCE AND THE ARTS.

(Abstract of Proceedings of Stated Meeting held Wednesday, November 1, 1922.)

Hall of the Institute,
Philadelphia, November 1, 1922.

Dr. H. J. M. Creighton *in the Chair.*

The following reports were presented for first reading:

No. 2793: Doctor Pfund's Physical Apparatus.
No. 2795: Johnson Hydraulic Valve.

R. B. Owens,
Secretary.

SECTIONS.

Section of Physics and Chemistry.—A joint meeting of the Section and the Philadelphia Section of the Illuminating Engineering Society was held in the Hall of the Institute on Thursday evening, October 5, 1922, at eight o'clock, with Dr. Howard Lyon in the Chair. The minutes of the previous meeting were approved as published.

Herbert E. Ives, Ph.D., of the Research Laboratories of the American Telephone and Telegraph Company and Western Electric Company, Incorporated, New York City, New York, presented a communication on "The Primary Standard of Light." A description was given of the use of the brightness of the black body at the melting point of platinum as a primary standard. The lecture was illustrated by means of apparatus and lantern slides.

The communication was discussed at length; a vote of thanks was extended to Doctor Ives; and the meeting adjourned. JOSEPH S. HEPBURN,
Secretary.

Section of Physics and Chemistry.—A meeting of the Section was held in the Hall of the Institute on Thursday evening, October 26, 1922, at eight o'clock, with Dr. George A. Hoadley in the Chair. The minutes of the previous meeting were read and approved.

Augustus Trowbridge, Ph.D., D.S.M., D.S.O., Chev.L.H., Professor of Physics in Princeton University, delivered a lecture on "High-speed Photography of Vibrations." A summary was given of the essential features of both the recording and the indicating members of apparatus designed to record accurately minute and rapid vibrations of various types, such as sound, electrical and mechanical. The apparatus was exhibited, and was used to produce records of both simple and complicated vibrations made during the course of the lecture.

The application of the apparatus to the study of the pressure and volume changes in the cylinder of the modern high-speed internal combustion engine was shown by means of lantern slides.

The paper was discussed; a vote of thanks was extended to Doctor Trowbridge; and the meeting adjourned. JOSEPH S. HEPBURN,
Secretary.

Section of Physics and Chemistry.—A meeting of the Section was held in the Hall of the Institute on Thursday evening, November 2, 1922, at 8 o'clock, with Dr. Thomas D. Cope in the Chair. The minutes of the previous meeting were approved as read.

Ludwik Silberstein, Ph.D., of the Research Laboratory of the Eastman Kodak Company, Rochester, New York, delivered a lecture on the "Spectrum of Neutral Helium and the Behavior of its Two Electrons" in which he demonstrated that the two electrons in a helium atom do not disturb each other to any appreciable extent, either electron being mainly controlled by the nucleus only.

The paper was discussed; a vote of thanks was extended to Doctor Silberstein; and the meeting adjourned. JOSEPH S. HEPBURN,
Secretary.

MEMBERSHIP NOTES.

ELECTIONS TO MEMBERSHIP.

(*Stated Meeting, Board of Managers, November 8, 1922.*)

RESIDENT MEMBERS.

DR. WALTER M. MITCHELL, 112 North 34th Street, Philadelphia, Pennsylvania.
MAJOR HARRY K. RUTHERFORD, Frankford Arsenal, Philadelphia, Pennsylvania.

NON-RESIDENT MEMBERS.

DR. GUSTAV EGLOFF, 1284-208 South La Salle Street, Chicago, Illinois.

ASSOCIATE.

MR. ROBERT ATKINSON, Haverford College, Haverford, Pennsylvania.

CHANGES OF ADDRESS.

MR. R. H. DAY, 505 W. Clapier Street, Philadelphia, Pennsylvania.
MR. W. L. GARRELS, Webster Groves, Route 5, Mason and Manchester Roads, St. Louis County, Missouri.
MR. FRANK GITTELSON, 3500 Holmes Avenue, Baltimore, Maryland.
MR. J. H. GRANBERY, American Car Company, Boston and Hudson Streets, Baltimore, Maryland.
MR. WALTER F. HAGAR, JR., in care of The Hagar Company, Ambler, Pennsylvania.
MR. T. C. MARTIN, Twinbrook Farm, Ringville, Massachusetts.
MR. C. P. SCHLICKE, 191 Berkeley Place, Brooklyn, New York.
MR. C. F. SULZNER, 131 N. E. Second Street, Miami, Florida.
MR. RALPH C. STEWART, Sydenham Building, 1512 Walnut Street, Philadelphia. Pennsylvania.
DR. C. C. THOMAS, 1111 Hollingsworth Building, Los Angeles, California.
MR. ROBERT L. WOOD, 218 South Sixteenth Street, Philadelphia, Pennsylvania.

NECROLOGY.

Mr. Morris Ebert, 1706 Green Street, Philadelphia, Pennsylvania.
Mr. A. L. Johnson, Mutual Life Building, Buffalo, New York.
Dr. John F. Kelly, 284 W. Housatonic Street, Pittsfield, Massachusetts.

LIBRARY NOTES.

PURCHASES.

BURGHARDT, H. D.—Machine Tool Operation, Part 2. 1922.
Encyclopædia Britannica, three supplementary volumes. 1922.
HOYT, J. E.—A Concise Physics for Engineering Students. 1922.
JONES, BENCE.—Royal Institution: Its Founder and Its First Professors. 1871.
Library Association.—Subject Index to Periodicals, 1917–1919. Part K, Science and Technology. 1922.
Royal Society.—Philosophical Transactions, Series A, volume 220. 1920.
Society for the Promotion of Engineering Education, Proceedings, vol. 29. 1922.

GIFTS.

American Association of Ice and Refrigeration, Proceedings of Annual Meeting, June 6 and 7, 1922. Chicago, Illinois, 1922. (From the Association.)

American Nickel Corporation, Pure Malleable Nickel. Clearfield, Pennsylvania, 1921. (From the Corporation.)

American Refractories Company, Arcofrax and Arcofrax (Pulverized), Bulletins on Bricks and Mortar. Pittsburgh, Pennsylvania, no date. (From the Company.)

Auburn Foundry Corporation, Auburn Hand Stokers and Clear-cut Grates. Auburn, Indiana, 1922. (From the Corporation.)

Badger Fire Extinguisher Company, Catalogue E, Badger Self-equalizing Expansion Joint. Boston, Massachusetts, 1922. (From the Company.)

Barrett Company, Roof Flashing Handbook. Philadelphia, Pennsylvania, 1922. (From the Company.)

Bartlett, C. O., and Snow Company, Photographs and Diagrams of Typical Installations, Bulletin 49. Cleveland, Ohio, 1922. (From the Company.)

Bologna R. Accademia Delle Scienze, Rendiconto, Classe di Scienze Fisiche, Nuova Serie: Vols. xxi, xxii, xxiii and Memorie Serie vii, Tomo iv, v and vi. Bologna, Italy, 1917, 1918 and 1919. (From the Academy.)

Brazil Ministerio da Agricultura, Industria e Commercio, Boletim Meteorologico, 1912 and 1913. Rio de Janeiro, Brazil, 1922. (From the Director.)

Bristol Company, Catalogue No. 1401 on Pyrometers. Waterbury, Connecticut, 1922. (From the Company.)

British Meteorological Committee, Meteorological and Magnetic Year-book, 1919, Part 3, Section 2, and Geophysical Journal, 1919. London, England, 1921. (From the Committee.)

British Reinforced Concrete Engineering Company, Limited, A Photographic Record of the Use of Reinforced Concrete in Modern Road Construction. Manchester, England, no date. (From the Company.)

Brown Instrument Company, Pamphlet of Brown Pyrometers. Philadelphia, Pennsylvania, 1922. (From the Company.)

Cadman, A. W., Manufacturing Company, Engineering Bulletins, Bearings and Bearing Metals and Cadman Metals. Pittsburgh, Pennsylvania, 1922. (From the Company.)

Canada Department of the Interior, Publications of the Dominion Observatory, Vol. v, No. 10, Gravity, and Vol. vi, Spectroscopic Investigations of the Sun. Ottawa, Canada, 1922. (From the Director of the Observatory.)

Canada Department of Mines, Report on Structural Materials along the St. Lawrence River, between Prescott, Ontario, and Lachine, Quebec. Ottawa, Canada, 1922. (From the Department.)

Carnegie Institute of Technology, General Catalogue, 1922–1923. Pittsburgh, Pennsylvania, 1922. (From the Institute.)

Carrier Engineering Corporation, The Weather Vein, February, March, May, June, September, October and November, 1921, and February to September, 1922. Newark, New Jersey. (From the Corporation.)

Central Station Steam Company, Cadillac Condensation Meter Catalogue No. 10. Detroit, Michigan, 1922. (From the Company.)

Century Electric Company, Single-phase Motors. St. Louis, Missouri, 1922. (From the Company.)

Clarkson Memorial College of Technology, Clarkson Bulletin Commencement Number, 1922. Potsdam, New York. (From the College.)

Davidson, M. T., Company, Catalogue A, "Davidson" Steam Pump. Brooklyn, New York, 1922. (From the Company.)

DeLaval Steam Turbine Company, Velocity Stage Turbines. Trenton, New Jersey, 1922. (From Dravo-Doyle Company, Philadelphia.)

Denver Rock Drill Manufacturing Company, Pamphlet on Waugh-Sinclair Portable Compressor Plant. Denver, Colorado, 1922. (From the Company.)

Drysdale and Company, Limited, Drysdale Electrically Driven Pumps for Boiler Feed Duty. Yoker, Glasgow, Scotland, 1922. (From the Company.)

Durst Manufacturing Company, Catalogue No. 24, Brass and Rubber Plumbing Goods. New York City, New York. (From the Company.)

Electrical Alloy Company, Electrical Heating Reference Data. Morristown, New Jersey, 1922. (From the Company.)

Electric Storage Battery Company, Bulletins of Exide Batteries for Starting, Lighting and Ignition Service of Automobiles. Philadelphia, Pennsylvania, 1922. (From the Company.)

General Electric Company, Reprint from *General Electric Review*, A New X-ray Diffraction Apparatus, by Wheeler P. Davey. Schenectady, New York, 1922. (From the Company.)

Gifford-Wood Company, Catalogue No. 31. Hudson, New York, 1922. (From the Company.)

Great Britain Royal Photographic Society, Illustrated Catalogue of the Sixty-seventh Annual Exhibition. London, England, 1922. (From the Society.)

Hamann, C. E., Charging Storage Batteries from A. C. Schenectady, New York, 1922. (From the General Electric Company.)

Harris, Samuel, and Company, Harris Reminder for October, 1922. Chicago, Illinois, 1922. (From the Company.)

Harvard University, Contributions from the Jefferson Physical Laboratory, Cruft High-tension Electrical Laboratory and Colleagues and Former Students, Dedicated to Professor Edwin Herbert Hall, Vol. xv, 1921. Cambridge, Massachusetts. (From the Jefferson Physical Laboratory.)

Hays, Joseph W., Corporation, Operating Instructions for the Hays Automatic Draft Recorder and Drafts and Draft Regulation. Michigan City, Indiana, 1922. (From the Corporation.)

Holophane Glass Company, Incorporated, Booklet No. 250, Scientific Street Lighting. New York City, New York, 1922. (From the Company.)

India Geological Survey, Records Vol. liv, Part I. Calcutta, India, 1922. (From the Survey.)

Institution of Civil Engineers, Transactions Vol. xlvi. Dublin, Ireland, 1922. (From the Institution.)

Ivanhoe-Regent Works, Catalogue No. 375, Blown and Pressed Design Ornamental Glassware Bowls, Shades, Enclosing Units. Cleveland, Ohio, 1922. (From the Works.)

Johnson and Phillips, Limited, Transformer Abstracts Nos. 11 and 12. London, England, 1922. (From the Company.)

Keeler, E., Company, Return Tubular Boilers, Cross Drum Water Tube Boilers, Water Tube Boilers and Keeler Boilers. Williamsport, Pennsylvania, 1922. (From the Company.)

Lewis Institute, Bulletins 9 and 10 on Quantities of Materials for Concrete and Wear Tests of Concrete. Chicago, Illinois, 1921. (From the Institute.)

London Meteorological Committee, Geophysical Memoirs No. 19, Hurricanes and Tropical Revolving Storms. London, England, 1922. (From the Committee.)

McCollum, Elmer V., The Newer Knowledge of Nutrition. New York City, New York, 1922. (From Philadelphia Interstate Dairy Council.)

Merchants' Association of New York, Year-book, 1922. New York City, New York, 1922. (From the Association.)

Michigan College of Mines, Year-book, 1921–1922, and Announcement of Courses, 1922–1923. Houghton, Michigan, 1922. (From the College.)

Miller, G. L., and Company, Semi-annual Survey, A Review of Building in the South. Atlanta, Georgia, 1922. (From the Company.)

National Carbon Company, Incorporated, The Technology of the Carbon-electrode Industry, by Charles L. Mantell. New York City, New York, 1922. (From the Company.)

National Metal Molding Company, Bulletins, National Metal Molding Conduits, and Liberty Rubber Covered Wire and Cable. Pittsburgh, Pennsylvania, 1922. (From the Company.)

National Research Council, Division of Engineering, Booklet of Information. New York City, New York, 1922. (From the Division of Engineering.)

New Hampshire Public Service Commission, Reports and Orders, Vol. viii, Advance Sheet No. 6. Concord, New Hampshire, 1922. (From the Commission.)

New York City Board of Water Supply, Report for 1921. New York City, New York, 1922. (From the Board.)

Northampton Polytechnic Institute, Announcements Educational and Social for the Session, 1922–1923. London, England, 1922. (From the Institute.)

Oberlin College, Laboratory Bulletins 23, 24 and 25. Oberlin, Ohio, 1922. (From the College.)

Ohio University, Catalogue Number of University Bulletin and Announcements for 1922–1923. Athens, Ohio, 1922. (From the University.)

Ontario Department of Mines, Thirtieth Annual Report, Vol. xxx, Parts III, IV, V and VI. Toronto, Canada, 1922. (From the Department.)

Ontario Hydro-electric Power Commission, Fourteenth Annual Report. Toronto, Canada, 1922. (From the Commission.)

Pennsylvania Department of Forestry, Guide to Forestry, Bulletin 26. Harrisburg, Pennsylvania, 1921. (From the Department.)

Pennsylvania Department of Labor and Industry, Monthly Bulletin, September, 1922. Harrisburg, Pennsylvania. (From the Department.)

Pennsylvania Hospital, Annual Report. Philadelphia, Pennsylvania, 1922. (From the Hospital.)

Pennsylvania Legislative Reference Bureau, Bulletin 23, The Township Law. Harrisburg, Pennsylvania, 1922. (From the Bureau.)

Pennsylvania State Highway Department, Report 1917–1920. Harrisburg, Pennsylvania, 1921. (From the Department.)

Pennsylvania Workmen's Compensation Board, Vol. vi, Report. Harrisburg, Pennsylvania, 1922. (From the Board.)

Power Turbo-blower Company, Catalogue 21, Power and Simplex Turbo-blowers and Turbines. New York City, New York, 1922. (From the Company.)

Princeton University, Catalogue 1921–1922. Princeton, New Jersey, 1922. (From the University.)

Reliance Manufacturing Company, Reliance Lock Washers Catalogue No. 6. Massillon, Ohio, 1922. (From the Company.)

Robertson, W. H. A., and Company, Limited, Shearing Machines, Reeling and Straightening Machines, Air Compressors, Rolling Mills and Wire Rope and Tube Drawing Machines. Bedford, England, no date. (From the Company.)

Sanderson Bibby Company, Limited, The Benn Patent Friction Clutch. London, England, 1922. (From the Company.)

Silica Gel Corporation, Refining and Recovery of Petroleum Oils. Baltimore, Maryland, 1922. (From the Corporation.)

Sly, W. W., Manufacturing Company, Dust, a Loss or a Gain. Cleveland, Ohio, 1922. (From the Company.)

Smith, Edgar F., Our Science and The Sodium Tungstates. Philadelphia, Pennsylvania, 1922. (From the Author.)

Smithsonian Institution of Washington, Remains of Birds from Caves in the Republic of Haiti, by Alexander Wetmore, and Remains of Mammals from Caves in the Republic of Haiti, by Gerrit S. Miller, Jr. Washington, District of Columbia, 1922. (From the Institution.)

South Dakota Board of Railroad Commissioners, Thirty-second Annual Report for 1921. Pierre, South Dakota, 1921. (From the Commissioners.)

Southern Railway Company, Twenty-eighth Annual Report. Richmond, Virginia, 1922. (From the Company.)

Superior Die Casting Company, Die Castings for Those Who Want Economy Plus Dependability. Cleveland, Ohio, 1922. (From the Company.)

Tokyo Imperial University, Calendar 1920–1921. Tokyo, Japan, 1921. (From the University.)

Trost Brothers, Bulletin on the Rotameter. Coventry, England, 1922. (From the Company.)

United Conveyor Corporation, Bulletin No. 105, United Steam Jet Conveyors. Chicago, Illinois, 1922. (From the Corporation.)

United States Air Service Engineering Division. Handbook of Instructions for Airplane Designers, Third Edition. Dayton, Ohio, 1922. (From Chief of Air Service.)

United States Bureau of Census. Fourteenth Census of the United States, 1920, Vol. vi, Part 3, Agriculture. Washington, District of Columbia, 1922. (From the Bureau.)

United States Commissioner of Lighthouses, Annual Report for the Fiscal Year Ended June 30, 1918. Washington, District of Columbia, 1918. (From the Commissioner.)

United States Department of Commerce, Statistical Abstract of the United States, 1921. Washington, District of Columbia, 1922. (From the Department.)

United States Steel Corporation, Speech of Hon. Will R. Wood, of Indiana, in the House of Representatives, Friday, June 23, 1922. Washington, District of Columbia, 1922. (From the Corporation.)

University of Michigan, Catalogue for 1921–1922 and Announcements for 1922–1923. Ann Arbor, Michigan, 1922. (From the University.)

Western Reserve University, Reports of the President and Other Officers for 1921–1922. Cleveland, Ohio, 1922. (From the University.)

Western Wheeled Scraper Company, Catalogue No. 53. Aurora, Illinois, 1922. (From the Company.)

Wolverine Motor Works, Incorporated, Crude Oil Engines. Bridgeport, Connecticut, no date. (From the Works.)

BOOK NOTICES.

THE ANALYSIS OF RUBBER, by John B. Tuttle. 158 pages and index, 8vo. New York, The Chemical Catalog Company. Price $2.50 net.

This is another volume of the American Chemical Society's Monograph Series, and follows as to size, type and general make-up, the previous volumes reviewed in this JOURNAL. The subject of the present work is one of great industrial and even social importance. The word "rubber," as applied to the materials now so familiar in the automobile tire, and long familiar in many other articles, is derived from its use in erasing lead pencil marks. The use in this sense dates from 1788, the pieces used for such purposes being termed "rubber" or "lead-killer." The latter uncouth phrase has fortunately been entirely forgotten. In the earlier uses, wild rubber, that is, the product of the plants growing without special care, was used, but to-day plantation rubber forms the bulk of the supply. In strict expression rubber is a polyterpene, an indefinite multiple of the ratio C_5H_8, but homologous forms exist. For each unit group of this formula there is one double carbon linking, and, therefore, the substance is capable of taking up certain negative elements. Upon this fact depends essentially the process of vulcanization. Many plants contain the rubber hydrocarbon or at least substances closely analogous. Even in temperate regions, milkweeds and spurges are frequently found containing such substances, but, of course, the low yield and the high cost of land and labor in such places precludes any exploitation, and even discourages scientific study. The hydrocarbons are generally found in a special system of vessels, the contents being classed by botanists as "latex." Of the tropical plants that yield a latex in such amount and of such quality as to constitute a commercial source, the *Hevea brasiliensis* Muell. Arg. is the most important. It belongs to the *Euphorbiaceæ,* a large group of plants, distributed over many parts of the world, many of which contain more or less latex. The specific name is spelled *Braziliensis* in the book, but the form *brasiliensis* is that used by botanical authorities and should be followed. English-speaking persons are apt to forget that the systematic names of plants and animals are not English words, but Latin, and should follow in orthography and orthoepy, as far as possible, the Latin forms. Hevea rubber is the best of the wild form and is now raised in the plantations. The growth of the plantation industry since 1903, when 25 tons were produced, to 1919 when 360,000 tons was the total, is shown in a table. Hevea rubber became known as Para rubber from the Brazilian port from which it was largely exported. The author of the work tells us that now-a-days cultivated rubber can be produced so cheaply that the poorer grades of wild rubber are but little sold, and even the better grades thereof have suffered from the competition of the plantation product. He thinks that in many cases the specifications, often insisted on, for Para rubber are not necessarily complied with.

While the main constituent of rubber is the hydrocarbon, small amounts of other substances are always present. Hevea rubber contains from 2 to 4 per cent. of resins, most of which are saponifiable and soluble in the common organic solvents. The best rubbers are clean and dry and have no appreciable ash. Rubber, of course, is liable to much adulteration. The vast array of articles manufactured from it are likely to contain many substances, some added properly in the course of manufacture, others as mere cheapeners. The analysis of commercial rubber and rubber products is, therefore, a complicated problem, but one to which a great amount of attention has been given and which to-day is in an advanced state of development. The extensive literature in journals and books has been gone over by the author and presented in this volume in compact form.

The present work is primarily addressed to the chemists in the laboratories of incidental consumers of rubber, but it is a comprehensive and careful summary of the trustworthy processes, and will be welcome to the more thoroughly trained chemists of the establishments concerned directly with the product. The field is very extensive and the enormous amount of data at hand has been sifted with care, giving to the worker a concise and large amount of information both as to the procedures and the nature and properties of the commercial forms of raw and manufactured articles.

One of the most important, perhaps really the most important step in the utilization of rubber, is the application of vulcanization. By this method many degrees of hardness can be obtained, and rubber thus became applicable to very many uses. Of course, the great boom in its use is due to the automobile, and it is interesting to note how the production of the raw material has kept pace with the demand. It is fortunate for the automobile industry that the plantation system has been capable of such great expansion.

Only limited space is given to the question of rubber substitutes. This matter is probably not of very great importance just now when the price of good rubber is low. Should the demand get materially in excess of the supply, renewed attention will be given to the research for substitutes or the synthetic production of the hydrocarbon. A bibliography is appended. It is extensive and arranged alphabetically by authors. It is a question whether such an arrangement is a good one. For any searching for particular data in the field, it seems that a classified list would be best.

HENRY LEFFMANN.

A CONCISE PHYSICS FOR ENGINEERING STUDENTS. By John E. Hoyt, Ph.D., assisted by Charles A. Bareuther, B.S., C.E., and N. M. Chamberlain, B.S., A.M. 385 pages, illustrations, 12mo. Philadelphia, P. Blakiston's Son and Company, 1922. Price, $2.50.

Anyone who undertakes to write a concise book on the subject of physics needs to be an adept in knowing what to omit.

When such a book is written for the purpose of being used as a text by students of engineering, there is an added difficulty on account of the fact that nearly all engineering is applied , ysics.

The subjects retained must be those of fundamental importance to the engineer and should be treated not only concisely, but with sufficient clearness to be readily understood.

The authors seem to have met these requirements, no small share of the credit being due to the extended lists of practical problems that are given for solution.

GEO. A. HOADLEY.

COLOUR INDEX, Part I. Edited by F. M. Rowe, D.Sc., F.I.C. 24 pages, quarto. Bradford, England, Society of Dyers and Colourists, 1922.

From the statement printed at the upper right-hand corner of several of the earlier pages, " Not to be bound with the completed volume," it is to be inferred that the present publication is rather suggestive than final. It is the initiative of a comprehensive catalogue of dyes especially arranged for users of these materials. Each dye is given a number, which does not agree with that given in the long-known " Tabellen " of Schultz, but in each case the Schultz number is given in parenthesis. It is not stated in the preface what motive has led to changing the numbers, but presumably it is the introduction of new dyes. Fast green O is number one in each list, and fast printing green, number 2, but the coincidence ceases at the latter point, and ultimately the difference becomes quite wide as 18 on the present list is 149 on Schultz. The scheme followed in the work is that now usual in such lists. Each dye is given a series of blocks with synonyms, scientific name and structural formula, when the latter is known, method of preparation, name of discoverer, important bibliography, general description, properties, and methods of use. The collection and arrangement of these data represents a great deal of labor, notwithstanding the tables and summaries already available. Extended tables are given of abbreviations for firm names, periodical literature cited and patent references. It is noted that the familiar BASF is here reduced to B. The type and printing are very satisfactory. The space limitations have necessitated a very small type in many entries, but these are easily readable. It is also to be noted that A. P. does not stand for American patent, but Austrian. What are commonly in this country called American patents are in this list designated U. S. P. Our government has officially adopted the term American as the designation in international affairs, such as our ambassadors, ministers and consuls, but some foreign nations, including Great Britain, have not accepted this plan, and in the diplomatic correspondence that took place during the war, some amusing see-sawing of official titles occurred.

The pamphlet in hand is, as noted, but a preliminary issue; the entire work will be extensive and useful. It will mark another step in enfranchisement from German control of the nations that constituted the group known as "The Allied and Associated Powers." Whether rivalries between these constituent nations will arise remains to be seen, but the economic struggle that was at the basis of the great war—and is at the basis of all wars—is influential in all countries. Circumstances often alter allies. However, the appearance of this pamphlet is a matter of congratulation by English-speaking chemists, and it is evident that it is the first pages of a very valuable and useful book.

HENRY LEFFMANN.

THE SUBJECT INDEX OF PERIODICALS, 1917–19. Issued by the Library Association. Part K, Science and Technology. London, The Library Association, 1922. 555 pages, 4to. Price, £1 15 schillings net.

Pope was in humorous mood when he noted

"How index learning turns no student pale,
But holds the eel of science by the tail,"

but the remark is a truism, for in the conditions of modern scientific development reference volumes, such as that under review, are absolutely necessary. The value of such works depends so largely upon the promptness of their appearance, that one is at first inclined to look with some disfavor upon an index extending only to three years prior to its appearance, but allowance must be made for several interfering conditions not the least of which has been the war. It is wise that the *terminus ad quem* should be the end of a calendar year, which necessitates waiting until the given year is completed. The collection and verification of the data will require a great deal of time, and the transcribing and printing will also delay publication. Accuracy in references and thoroughness in scanning the literature are, of course, of primary importance, but in recent years these procedures have been carefully followed and the indexes now before the public are mostly quite satisfactory.

The volume before us is one of a series which is presumably intended to cover a very wide range of literature. K, the section in hand, is devoted to Science and Technology. It contains an enormous number of entries clearly and conveniently arranged. A slip attached to the title page states that there is a total of 15,000 entries obtained from the examination of more than 400 periodicals. The references are classified by subjects arranged alphabetically. A high degree of subdivision with the use of a very distinct type for all headings greatly aids the searcher, and adds to the value of the book. The work is highly creditable to all who have had a share in its production.

HENRY LEFFMANN.

LE BEAU, LE MAUVAIS TEMPS ET LA RELATIVITÉ, par P. Drosne. 68 pages, 4½" x 7", paper. Paris, Gaston Doin, 1922. Price, 3 Francs 50 net.

Relativity is the fashion, in fact, scientific minds have recognized fully that a new doctrine has appeared, under conditions in some respects extremely modest and yet in others, courageous. According to M. Drosne the indisputable and undisputed point is that the classic science (meteorology) has arrived at a decisive turning point in its history. He has endeavored to show the enormous progress which will be obtained when it is decided to state its problems in terms of relativity. In his opinion it is not "till then that we will know what we are saying and what we are calculating. No relativity, no salvation."

NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS. Report No. 150, Pressure Distribution over Thick Aerofoils. Model Tests by F. H. Norton and D. L. Bacon. Langley Memorial Aeronautical Laboratory. 22 pages, illustrations, quarto. Washington, Government Printing Office, 1922.

This investigation was undertaken in order to study the distribution of loading over thick wings of various types. The loading on the wing was determined by taking the pressure at a number of holes on both the upper and lower surfaces of a model wing in the wind-tunnel. The results from these tests show, first, that the distribution of pressure over a thick wing of uniform section is very little different from that over a thin wing; second, that wings tapering either in chord or thickness have the lateral centre of pressure, as would be expected, slightly nearer the centre of the wings; and, third, that wings tapering in plan form and with a section everywhere proportional to the centre section may be considered to have a loading at any point which is proportional to the chord when compared to a wing with a similar constant section. These tests confirm the belief that wings tapering both in thickness and plan form are of considerable structural value because the lateral centre of pressure is thereby moved toward the centre of the span.

Report No. 154, A Study of Taking-off and Landing an Airplane, by T. Carroll. Langley Memorial Aeronautical Laboratory. 7 pages, illustrations, quarto. Washington, Government Printing Office, 1922.

This report covers the results of an investigation carried on at the Langley Memorial Aeronautical Laboratory for the purpose of discussing the various methods of effecting the take-off and the landing of an airplane, and to make a direct analysis of the control movements, the accelerations, and air speeds during these manœuvres. The recording instruments developed at the laboratory were used in this test and the records obtained by them were made the basis of a comparative study of the two extreme methods of taking-off (the tail-high and the tail-low methods) and of various types of landings. It is believed that this is the first time that an accurate record has been obtained of the movements of the controls during these important manœuvres, and the records are of further interest from the fact that they were taken synchronously with records of the air speed and acceleration.

The records themselves should be of considerable value to a student pilot in enabling him to visualize the movements of the controls and the consequent effect upon the air speed and acceleration. This opens a very important field for research in the study of the technic of piloting, either of student pilots or for the "refresher" courses or other checking up of pilots in general. With these instruments it will be possible to obtain records of the manœuvring of any pilot in practically any type of airplane, and from the records so obtained any fault or roughness can be immediately noted. This can be done not only in the manœuvres of taking-off or landing, but in any sort of straight flight or "stunting."

PUBLICATIONS RECEIVED.

Méthodes et Problémes de Théorie des Fonctions, par Émile Borel. 148 pages, illustrations, 8vo. Paris, Gauthier-Villars et Cie., 1922. Price 12 Francs.

Cours de Physique Mathématique de la Faculté des Sciences, par J. Boussinesq. Compléments au Tome III. 217 pages, 8vo. Paris, Gauthier-Villars et Cie., 1922. Price 30 Francs.

Library Association: The Subject Index to Periodicals, 1917–1919. Part K, Science and Technology. 555 pages, quarto. London, The Library Association, 1922. Price £1 15s. net.

Society of Dyers and Colourists: Colour Index. Part I. Section A, Synthetic Organic Dyestuffs. 24 double pages, quarto. Bradford, England, Society, 1922.

A Concise Physics for Engineering Students, by John E. Hoyt, Ph.D., assisted by Charles A. Bareuther, B.S., C.E., and N. M. Chamberlain, B.S., A.M. 385 pages, illustrations, 12mo. Philadelphia, P. Blakiston's Son and Company, 1922. Price $2.50.

Canada Department of Mines, Mines Branch: Report on Structural Materials along the St. Lawrence River, between Prescott, Ontario, and Lachine, Quebec, by Joseph Keele and L. Heber Cole. 119 pages, illustrations, plates, maps, 8vo. Ottawa, King's Printer, 1922.

Water Supply Installations for Farmsteads and Country Estates, by William Paul Gerhard, C.E., Dr.Eng. 24 pages, 8vo. New York, Author, 1922. Price forty cents.

U. S. Bureau of the Census: Fourteenth Census of the United States. Manufactures: 1919. Machinery, Textile Machinery and Machine Tools. Prepared under the supervision of Eugene F. Hartley, Chief Statistician for Manufactures. 20 pages, quarto. Washington, Government Printing Office, 1922.

United States Public Health Service: Physiological Effects of Exposure to Low Concentrations of Carbon Monoxide, by R. R. Sayers, F. V. Meriwether and W. P. Yant. Reprint No. 748 from the Public Health Reports. 16 pages, plate, 8vo. Washington, Government Printing Office, 1922. Price five cents.

Technical Books of 1921: A selection, compiled by Donald Hendry, Head of the Applied Science Reference Department, Pratt Institute Free Library, Brooklyn, New York. 28 pages, 16mo. Brooklyn, New York, Pratt Institute Free Library, 1922.

National Advisory Committee for Aeronautics: Technical Notes No. 115, The Effect of Longitudinal Moment of Inertia upon Dynamic Stability, by F. H. Norton and T. Carroll, Langley Memorial Aeronautical Laboratory. 3 pages, photograph, quarto. No. 116, F-5-L Boat Seaplane. Comparative Performance with Direct Drive and Geared Engines. Compiled by Lieut. W. S. Diehl, Bureau of Aeronautics, U. S. N. 12 pages, quarto. Washington, Committee, 1922.

CURRENT TOPICS.

The Curve of Energy Distribution in the Ultra-violet Part of the Solar Spectrum. C. Fabry and H. Buisson. (*Comptes Rendus,* July 17, 1922.)—"The distribution of energy in a continuous spectrum can be determined by using some thermometric instrument as the apparatus for measuring the energy. This direct method necessitates the employment of delicate apparatus and cannot be applied except under conditions rarely realized in our laboratories. Moreover, the thermometric arrangement for receiving energy has only a feeble power of definition. This is in itself a grave drawback in the study of the solar spectrum, which is crossed by absorption lines that are very close together in places. These difficulties explain why the energy curve of the solar spectrum is so little known in the region of small wave-lengths where the experimenter is confronted by the presence of but a small amount of energy in a spectrum having numerous dark lines and by a strong absorption by the earth's atmosphere. Abbot's measurements, which are the most complete of all those made on the solar spectrum, are very uncertain in this part of the spectrum."

It is for such reasons that the French savants have selected for their work a method less direct, it is true, but more easy and certain in its application. They proceeded by making comparisons with an artificial source of radiation of which the energy distribution curve was known. The intensities of the light from the two sources were compared for several wave-lengths and from their ratio at a selected wave-length and the known energy of one source it was possible to calculate the energy of the other for that frequency. Many sources of error drop out of consideration in this method, but it is required to know thoroughly the energy distribution of the standard with which comparison is made. Fortunately the law of radiation of a black body is well known and certain solid bodies are sensibly identical in their radiation with a black body. Such a solid is the positive crater of the electric arc, and 3750° was taken as its temperature. On the slit of the spectrograph were projected in turn the image of the crater and that of the sun. The intensity of the latter could be reduced in a known proportion by the use of diaphragms or of absorbing screens. The opacity of the two images on the photographic plate was measured by a microphotometer and from the results was calculated the ratio of the intrinsic brightness of the two sources of light. At different hours of the same day the comparison was repeated in order that the coefficient of atmospheric absorption might be determined and that, further, the intensity of the sunlight outside of the atmosphere might be computed.

Determinations were made for five wave-lengths ranging from

3940 to 2922. The coefficients of atmospheric absorption had a corresponding range from .32 to 4.82. The significance of this last figure is the following. When sunlight is passing vertically down through the air, only one part in 70,000 of the energy at wave-length 2922 gets to the surface of the earth.

From each of the five comparisons the temperature of the sun is deduced in terms of the absolute scale. The highest value is 6016° and was got from the longest wave-length while the lowest 5832° came from the third of the five. The next-to-highest temperature was derived from the shortest wave-length.

Below the wave-length 2900 all observation is impossible by reason of the enormous atmospheric absorption. There seems to be no reason for hesitating to assume, even in the absence of actual measurements, that the sun emits wave-lengths shorter than 2900 about as a black body at the temperature of 6000° abs. emits them. " If this be so, the importance of the radiation that cannot be observed is far from negligible. The energy emitted by the sun in the form of radiation having wave-lengths inferior to 2900 is one-twenty-fourth of its total radiation and about one-quarter of its total radiation is ultra-violet, that is, of wave-length less than 4000 Angstrom units." G.F.S.

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